S
333.91
W31r191

STATE DOCUMENTS COLLECTION

AUG 18 2000

MONTANA STATE LIBRARY
1515 E. 6th AVE.
HELENA, MONTANA 59620

Fate and Mobility of Arsenic in Soils of the Madison River Basin

Report #191

MONTANA
University System

WATER RESOURCES
CENTER

Submitted as three articles

(Reprinted with the permission of the Journal of Environmental Quality.)

Jones, C.A.,, Inskeep, W.P., and D.R. Neuman, 1997, Arsenic Transport in Contaminated Mine Tailings following Liming, Vol. 26 no. 2, March-April, 26:433-439.

Darland, J.E., and W.P. Inskeep, 1997, Effects of pH and Phosphate Competition on the Transport of Arsenate, Vol. 26, no.. 4, July-August, 26:1133-1139.

Jones, C.A., Inskeep, W.P., Bauder, J.W., and K.E. Keith, 1999, Arsenic Solubility and Attenuation in Soils of the Madison River Basin, Montana: Impacts of Long-Term Irrigation, Vol. 28, no. 4, July - August, 28:1314-1320.

Also on *MONTANA WATER* at

http://water.montana.edu/programs/research/MWC/abstracts/abstracts8.html#191

ABSTRACT #191

Arsenic contamination of surface and ground waters is an important problem in many watersheds in Montana, either as a result of natural processes or mining activities. The Madison River in Southwestern Montana contains elevated As concentrations (100 to 300 ug L-1) as a result of natural geothermal sources near its headwaters. Previous studies have concluded that irrigation with Madison River water may be responsible for contamination of domestic wells near Three Forks, MT. The objectives of this study were to (I) determine sorption capacities of irrigated and nonirrigated soils of the Madison River basin, (ii) evaluate the potential role of redox reactions on the solubility and subsequent transport of As through soils, and (iii) determine effects of pH and phosphate on As transport. Sorption experiments conducted under batch conditions showed that Madison River soils with long-term irrigation histories had sufficient As sorption capacity to retain As applied in irrigation water. Furthermore, As sorption was lowest in those soils which supported a lower redox status. In these conditions, a significant fraction of the total soluble As was present as arsenite rather than arsenate. Controlled redox experiments with Madison River soils and representative solid phases showed that the solubility of As increases as redox levels approach 0 mV. Column experiments showed that the transport of As increased with increasing pH especially at pH values exceeding 8-8.5. and at P:As molar ratios exceeding 10:1. The amount of As transported through columns containing a representative aquifer sand was a function of column pore water velocity: As recovered in the effluent increased with increasing pore water velocity, indicating that As sorption reactions were kinetically limited during transport. Results from these studies indicate that redox conditions, pH, phosphate concentration and pore water velocity all play important roles in the amount of As transported through soils.

DEC 08 1999

December 1, 1999

MONTANA
University System
WATER RESOURCES
CENTER

Copyright Editor
Journal of Environmental Quality
677 S. Segoe Road
Madison, WI 53711

RECEIVED
DEC 13 1999

RE: Permission to reprint/publish 3 articles

Greetings!

The 3 articles listed below are the result of an original Montana Water Center 'seed' research project begun in FY94. Based on the success of this initial work, the P.I.s were successful in obtaining additional funding to expand their project.

Journal of Environmental Quality

- Jones, C.A.,, Inskeep, W.P., and D.R. Neuman, 1997, *Arsenic Transport in Contaminated Mine Tailings following Liming,* Vol. 26 no. 2, March-April, 26:433-439.
- Darland, J.E., and W.P. Inskeep, 1997, *Effects of pH and Phosphate Competition on the Transport of Arsenate*, Vol. 26, no.. 4, July-August, 26:1133-1139. (acknowledges Water Center)
- Jones, C.A., Inskeep, W.P., Bauder, J.W., and K.E. Keith, 1999, *Arsenic Solubility and Attenuation in Soils of the Madison River Basin, Montana: Impacts of Long-Term Irrigation*, Vol. 28, no. 4, July - August, 28:1314-1320. (acknowledges Water Center)

An initial Water Center funding request is that P.I.s *".... publish their findings in a technical journal of their choice."* As part of its mandate, the Center also includes a copy of these findings in its 'Technical Reports Library' - a small collection maintained here at the Center and at Montana university libraries. **What I need from you is your permission to publish and/or reprint these articles as part of**

> ***Montana University System Water Center Technical Report Series - #191- Fate and Mobility of Arsenic in Soils of the Madison River Basin.***

An average of 30 photocopies will be made for distribution free of charge. *Typical users of our Technical Report Library are university faculty/staff, agency professionals, scientists, and engineers from throughout Montana.* FYI - abstracts of most of our reports are available on the WEB at http://water.montana.edu/docs/reports.html

Could you please send the necessary 'permissions to publish' forms? Thanks for taking the time on this. Please call or e-mail me if you have any further questions.

Sincerely,

Kathy Stephens

Kathy Stephens, Section 104(B) Program Manager
ph: 406-994-1772
Visit MONTANA WATER at http://water.montana.edu

12/9/99
Permission granted.
DAVID M. KRAL
Assoc. Exec. V.P.

stephens@montana.edu

cc: Dr. William Inskeep

C:\Main\Pubs\inskeep-jrnl-env.quality.wpd

Dorothy Bradley, Director
Huffman Building 101
P.O. 172690
Montana State University
Bozeman, MT 59717-2690
Fax 406-994-1774
Tel. 406-994-6690
E-mail wwwrc@gemini.oscs.montana.edu
Web Site http://www.montana.edu/wwwrc

Marvin Miller, Assoc. Director
Montana Bureau of Mines
Montana Tech
1300 W. Park Ave.
Butte, MT 59701-8997
Fax 406-496-4451
Tel. 406-496-4155
E-mail marv@mbmgsun.mtech.edu

Don Potts, Assoc. Director
School of Forestry
University of Montana
Missoula, MT 59812
Fax 406-243-4510
Tel. 406-243-5522
E-mail fo_dfp@selway.umt.edu

Reprinted from the *Journal of Environmental Quality*
Volume 26, no. 2, March–April 1997, Copyright © 1997, ASA, CSSA, SSSA
677 South Segoe Rd., Madison, WI 53711 USA

Arsenic Transport in Contaminated Mine Tailings following Liming

C. A. Jones, W. P. Inskeep,* and D. R. Neuman

ABSTRACT

The practice of liming to remediate contaminated soils and mine tailings has the potential to mobilize arsenic (As), due to the pH dependence of As sorption reactions on oxide minerals and layer silicates. The objectives of this study were to determine the effects of liming on As mobility in mine tailings and identify possible mechanisms controlling As mobilization with increased pH. Six mine tailing samples obtained from an abandoned copper smelter near Anaconda, Montana were analyzed for total As and soluble constituents using saturated paste extractions. Concentrations of soluble As among the six samples did not correlate with total As, but were more closely related to pH. Saturation indices with respect to known metal arsenate solid phases suggested that metal arsenate solid phases were not controlling soluble As in these samples. Two low pH samples (pond tailings and reprocessed tailings) were chosen for more detailed chemical characterization and unsaturated column transport experiments before and after liming. Soluble As concentrations measured in column effluent increased by factors of 10 (reprocessed tailings, RT) to 400 (pond tailings, PT) following liming. Sequential extractions of these tailing samples showed that the PT contained significantly higher "labile" As relative to the RT, consistent with amounts of As mobilized after liming. Further characterization of these samples using scanning electron microscopy (SEM) and energy dispersive analysis of x-rays (EDAX) suggested that these samples do not contain discrete metal arsenate solid phases. Based on this suite of experimental data, increased mobility of As with liming appears to be consistent with the pH dependence of sorption reactions of As on Fe oxide minerals rather than dissolution-precipitation reactions involving As.

Liming is an established, effective method for immobilizing trace metals, elevating pH, and promoting plant reestablishment in low pH, contaminated mine tailings (Neuman et al., 1993b); however, increases in soil pH may result in As mobilization because of the pH dependence of sorption reactions. This raises the concern of contaminating drinking water supplies following liming in soils or tailings containing elevated levels of As that are hydraulically connected to groundwater or surface water. The USEPA may reduce the maximum contaminant level for As in drinking water from 0.67 μM to between 0.0067 and 0.134 μM, due to recent evidence that the current criteria may result in human cancer risks as high as 13 in 1000 (Pontius et al., 1994). Consequently, there is significant interest in processes controlling the transport of As into surface or groundwaters.

Previous studies have investigated the pH effects of As sorption on soils or well-characterized solid phases (Hingston et al., 1971; Goldberg and Glaubig, 1988). Goldberg and Glaubig (1988) found that the sorption of arsenate by montmorillonite and kaolinite was highest near pH 5 and dropped significantly between pH 7 and 9. Hingston et al. (1971) determined that arsenate sorption on both goethite and gibbsite decreased with increasing pH. Goldberg (1986) reported good correlations between experimental and modeled arsenate sorption on Fe and Al oxides using a constant capacitance model, which assumed a ligand exchange mechanism. Jacobs et al. (1970) showed that the elimination of amorphous Fe and Al by treatment with oxalate substantially reduced or eliminated arsenate sorption capacity in 24 Wisconsin soils, implying soil arsenate was primarily sorbed to oxides of Fe and Al. In contrast, arsenate solid phases are generally believed to be nonexistent in surface soils, due to their relatively high solubility, except at high arsenate levels (Robins, 1981; Sadiq et al., 1983; Dove and Rimstidt, 1985; Nishimura et al., 1987). For example, Dove and Rimstidt (1985) found that at an Fe activity of 1 mM, arsenate activities needed to be at least 0.01 M for scorodite ($FeAsO_4 \cdot 2H_2O$) to be stable, which is much higher than typically found in soil porewater. Thus, the effects of pH on arsenate solubility in soils are due primarily to surface complexation reactions rather than precipitation-dissolution reactions.

One of the recommended liming strategies for maximum metal immobilization in mine tailings of the Clark Fork River Basin of Montana consists of raising the soil pH to near 10, using a mixture of $Ca(OH)_2$ and $CaCO_3$ and allowing the soil to equilibrate for approximately 1 yr prior to plant reestablishment. During equilibration, the pH generally declines to values near 8 (Schafer et al., 1989). Field research at contaminated mining sites in the Clark Fork Basin has shown that this liming strategy results in metal immobilization, yet may lead to As mobilization (Neuman et al., 1993a).

The objectives of the present study were to: (i) determine the extent of As mobilization in low pH mine tailings after liming and (ii) evaluate probable mechanisms for increased As transport after liming. To accomplish these objectives, several representative mine tailings and metal-contaminated soils were characterized and two of the tailings were subjected to transport experiments with and without liming.

MATERIALS AND METHODS

Sample Collection and Characterization

Six samples (0 to 0.30-m depth) were collected within 2 km of an abandoned copper smelter located in Anaconda, MT, and included pond tailings (PT), smelter stack deposits (SSD), and reprocessed tailings (RT). All sampling locations were

---

C.A. Jones and W.P. Inskeep, Dep. of Plant, Soil and Environmental Sciences; D.R. Neuman, Reclamation Research Unit, Montana State Univ., Bozeman, MT 59717. Contribution of the Montana Agric. Exp. Stn., Journal no. J-5095. Received 17 Jan 1996. *Corresponding author (usswi@msu.oscs.montana.edu).

Published in J. Environ. Qual. 26:433-439 (1997).

Abbreviations: SEM, scanning electron microscopy; EDAX, energy dispersive analysis of x-rays; SSD, smelter stack deposits; RT, reprocessed tailings; DOC, dissolved organic carbon; ICP, inductively coupled plasma spectrometry; IC, ion chromatography; CB, citrate bicarbonate; CDB, citrate dithionite bicarbonate; PT, pond tailings

within a site that was placed on the National Priority List in 1983 due to metal contamination following 96 yr of copper smelting (Neuman et al., 1993b). Samples were collected in triplicate at two locations. Concentrations of total As and total cations (Ca, Cu, Fe, Mn, Pb, and Zn) were determined using x-ray fluorescence (Jones, 1982) and particle size analysis was performed using the hydrometer method (Gee and Bauder, 1986). Saturated pastes (Rhoades, 1982) were centrifuged at 10 000 *g* and filtered through 0.20-μm nylon filters to characterize soil solution chemical content. The resulting filtrates were analyzed for dissolved organic carbon (DOC) using a Dohrmann DC 190; cations, B, and S by inductively coupled plasma spectrometry (ICP); and Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-} by ion chromatography (IC). Total alkalinity was measured by HCl titration to an inflection point near pH 4.5. These titrated samples were then sparged with N_2 (g) for more than 15 min, titrated to the original pH with NaOH, and retitrated to the inflection pH with HCl to calculate carbonate and noncarbonate alkalinity. Continuous-flow hydride generation atomic absorption spectrophotometry (HG-AAS) was used to analyze As. Samples were acidified to 3*M* HCl, prereduced with 1% KI, and treated with both 5*M* HCl and 0.6% sodium borohydride ($NaBH_4$) in 0.5% NaOH. Flow rates were approximately 7 and 1 mL min^{-1} for samples and reagents, respectively. Generated arsine was quantified at 193.7 nm in an air-acetylene flame (Perkin Elmer 3100). The As detection limit, estimated as three standard deviations of 50 absorbance blank readings, was 3.4 n*M*. Free ion activities were estimated using the aqueous chemical equilibrium model, GEOCHEM (Sposito and Mattigod, 1979) as modified by Parker et al. (1987). Stability constants for pertinent aqueous complexes were obtained from compiled thermodynamic equilibrium data (Sadiq and Lindsay,1979; Sposito and Mattigod, 1979; Nordstrom and May, 1989).

Each sample was subjected to a sequential extraction for As (Johnston and Barnard, 1979; Ganje and Rains, 1982) based on developed procedures for extraction of P (Olsen and Sommers, 1982) and organically bound metals (Tessler et al., 1979). Although sequential extractions yield only qualitative information on As fractionation, this procedure was useful for assessing the relative lability of As among the different samples. The method consisted of sequential extractions in the following order: 1 *M* NH_4Cl, 0.1 *M* NaOH, 0.3 *M* citrate bicarbonate (CB), 0.3 *M* citrate dithionite bicarbonate (CDB), 1 *M* HCl and 30% H_2O_2/0.8 *M* NH_4OAc. All samples were analyzed for As with HG-AAS; the CDB and H_2O_2 extracts were also analyzed with ICP. The residual solids were digested using a four acid heat-treatment (Welsch et al., 1990) and As levels in the resulting digests were determined using HG-AAS.

Selected grains of PT and RT were affixed to Al stubs and coated with C for viewing with a scanning electron microscope (SEM). The grains were mapped for 15 elements using Energy Dispersive Analysis of x-rays (EDAX) to identify particles enriched in As, Fe, or S. Particles that contained high levels of these elements were analyzed in further detail to determine semiquantitative atomic ratios using standardless analysis with PROZA correction (Goldstein et al., 1992).

Column Experiments

Unsaturated column experiments were conducted on limed and unlimed PT and RT. Liming treatments consisted of adding a mix of 60% $CaCO_3$/40% $Ca(OH)_2$ at concentrations of 3.0 and 25.6 g kg^{-1} of PT and RT, respectively. The $CaCO_3$/$Ca(OH)_2$ ratio and liming concentrations were determined from acid-base accounting as part of a remedial investigation study (Schafer et al., 1989). The PT (25% sand, 56% silt, 19% clay) was diluted 3:1 with 40 to 200 mesh SiO_2 (Fluka) to assure adequate flow, whereas the RT (95% sand, 3% silt, 2% clay) was left undiluted. Columns (5 cm diam., 20 cm long PVC pipe) were sealed with rubber O-rings in polycarbonate end caps. A plastic porous plate (Soil Measurement Systems, Tucson, AZ) was inserted within each bottom end cap to control soil matric potential. Soil columns were packed by tapping lightly between successive soil additions and then were saturated from the bottom with 5 m*M* K_2SO_4. Upon complete wetting, a 20 kPa vacuum was applied to the bottom of the column, and 5 m*M* K_2SO_4 was delivered to the top of the column at 10 mL h^{-1} with a syringe pump. This flow rate equates to a pore water velocity of approximately 1.7 cm h^{-1}. The vacuum was adjusted over the course of the experiments to maintain volumetric water contents (θ_V) between 30 to 36% and 23 to 28% for the PT and RT, respectively. These water contents were well below the saturated water contents in each respective column. Under these conditions the columns remained aerated and it was assumed that soluble As was present as arsenate (As[V]) rather than arsenite (As[III]). Unlimed control columns were sampled for approximately 23 and 100 pore volumes for the PT and RT, respectively, then treated with a high pH influent (0.1 *M* $KHCO_3$, adjusted to pH 10.1 with KOH, and bubbled with air to maintain the pH level). All effluent samples were analyzed for pH, EC, As, and alkalinity. Selected samples were also analyzed for Fe, Ca, S, Cu, and Zn, and a smaller subset analyzed for K, Mn, Al, Na, and Mg. Analysis methods were identical to those outlined previously. Free ion activities were calculated using GEOCHEM on those samples analyzed for the complete parameter set, as well as selected samples which produced reasonable cation/anion balances without data on K, Mn, Al, Na, and Mg.

Table 1. Total arsenic and metal concentrations of six mine samples determined by x-ray fluorescence (XRF).

Element	Pond tailings (PT) A	Smelter stack deposits (SSD) B	C	D	Reprocessed tailings (RT) E	F
	mg kg^{-1}					
As	248	2 358	48	1 506	3 421	2 338
Ca	ND†	27 900	21 100	20 700	14 800	5 300
Cu	274	1 331	126	616	2 386	2 382
Fe	13 100	46 800	42 800	35 400	215 800	152 300
Mn	626	1 283	1 203	885	914	ND
Pb	704	301	ND	147	881	813
Zn	103	816	205	466	341	671

† ND = none detected.

RESULTS AND DISCUSSION

Sample Characterization

Total As contents of the six mine samples (Table 1) ranged from 48 to 3421 mg kg^{-1} (10–700-fold higher than typical background levels of 5 mg kg^{-1}; Nriagu, 1994). Iron represented 15 to 21% of the RT, indicative of high initial pyrite (FeS_2) content. Total metal concentrations of Cu, Pb, and Zn were also generally elevated, consistent with the composition of mine tailings in this region. Stabilization of these barren tailings through revegetation has been a primary goal of mine reclamation efforts to reduce erosion and prevent migration of these contaminants to receiving waters.

Table 2. Soil water chemistry of saturated paste extracts for six mine soils and saturation indices† with respect to selected solid phases.

Constituent	Pond tailings (PT)	Smelter stack deposits (SSD)			Reprocessed tailings (RT)	
	A	B	C	D	E	F
% Saturation, mass basis	37	29	27	25	24	24
pH	4.1	7.8	8.0	7.8	3.5	3.9
E.C., dS/m	1.52	0.62	0.35	0.36	2.79	2.56
DOC, m*M* as C	3.8	2.5	1.7	0.8	0.3	0.4
Noncarb. alk., m*M* charge	0	2.0	0.3	0.9	0	0
Cations						
K, m*M*	0.31	0.17	0.11	0.04	0.08	0.19
Ca, m*M*	5.19	2.08	0.85	1.14	13.68	13.97
Mg, m*M*	1.28	1.08	0.47	0.43	0.41	0.40
Na, m*M*	0.48	0.80	0.71	0.66	0.10	0.12
Al, μ*M*	149	<7	<7	<7	1067	360
Fe, μ*M*	26	0.4	<0.30	<0.30	375	899
Mn, μ*M*	269	1.8	<0.05	<0.05	73	39
Zn, μ*M*	304	0.9	0.5	0.2	746	767
Cu, μ*M*	510	2.8	1.0	1.8	528	502
Pb, μ*M*	<0.41	<0.41	<0.41	<0.41	0.62	1.20
Ni, μ*M*	0.97	<0.37	<0.37	<0.37	6.00	3.53
Cr, μ*M*	0.35	<0.27	<0.27	<0.27	0.56	0.65
Cd, μ*M*	1.09	<0.05	<0.05	<0.05	0.96	1.61
Anions, m*M*						
As	0.0007	2.32	0.02	0.64	0.0003	0.0001
B	0.007	0.005	0.003	0.007	0.018	0.019
Cl	0.27	0.10	0.14	0.05	0.06	0.05
HCO_3	0.00	1.33	2.11	0.74	0.00	0.00
NO_3	0.33	0.40	0.46	0.19	0.07	0.05
PO_4	ND‡	0.03	ND	0.01	ND	ND
SO_4	8.26	1.51	0.26	0.67	18.22	13.30
Charge balance§						
Σcationic charge, m*M*(+)	12.36	5.07	3.81	3.40	20.85	21.80
Σanionic charge, m*M*(−)	12.06	5.13	2.44	2.41	27.19	21.28
Net charge, m*M*	0.30	−0.06	1.37	0.98	−6.34	0.52
% error, as cationic chg.	2.4	−1.1	35.9	29.0	−30.4	2.4
Saturation indices						
$Al(AsO_4)$	−5	−8	−10	−8	−7	−7
$Ca_3(AsO_4)_2$	−23	−5	−9	−6	−26	−25
$Cu_3(AsO_4)_2$	−9	−1	−7	−2	−13	−12
$Fe(AsO_4)$	−4	−3	−8	−5	−4	−3
$Mg_3(AsO_4)_2$	−23	−4	−8	−6	−28	−27
$Mn_3(AsO_4)_2$	−16	−4	−13	−11	−22	−22
$Zn_3(AsO_4)_2$	−17	−7	−11	−9	−20	−19

† Saturation index = log [IAP(ion activity product)/K_{sp}]; K_{sp} values from Wagemann (1977).

‡ ND = none detected.

§ Charge balance determined from distribution of ion species (GEOCHEM).

The chemical content of saturated paste extracts for the six mine tailing samples is shown in Table 2. The SSD had saturated paste pH values ranging from 7.8 to 8.0, whereas the PT and RT had pH levels of 3.5 to 4.1. As expected, soluble concentrations of nearly all metal ions were highest in those samples with low pH, with SO_4^{2-} being the principal anion. High soluble concentrations of Zn, Cu, Ni, Cr, and Cd in the low pH samples document the need for liming to reduce potential soluble metal migration and phytotoxicity. Conversely, the SSD had relatively low soluble metal concentrations, balanced primarily with the anions HCO_3^-, SO_4^{2-}, and $HAsO_4^{2-}$. Soluble As concentrations for the six soils spanned more than four orders of magnitude, and were positively correlated with pH. The relationship between soluble As and pH among all samples is consistent with the pH dependence of As sorption reactions on oxide minerals and layer silicates (Goldberg, 1986; Goldberg and Glaubig, 1988). Total As did not correlate well with soluble As; for example, RT samples had the highest total As but the lowest soluble As.

Charge balance calculations performed after GEOCHEM speciation yielded errors ranging in magnitude from 1.1 to 35.9% (Table 2). A comparison of ion activity products (IAPs) for seven possible metal arsenates with their respective literature K_{sp} values (Wagemann, 1977), indicated that all six saturated pastes were undersaturated with respect to metal arsenates. Given discrepancies in literature K_{sp} values (Robins, 1981; Sadiq and Lindsay, 1981; Robins, 1987), and uncertainty regarding the extent that true equilibrium was reached during the 24-h saturated paste extraction, it cannot be definitively concluded from IAP calculations that metal arsenates did not exist in these samples. Dissolution studies with metal arsenates (Ca, Fe, and Mg) show that As and metal activities can vary up to approximately twofold after 24 h from calculated equilibrium activities (Robins, 1981). At most, this could account for errors in log (IAP/K_{sp}) of 0.6 to 1.5 for Ca, Fe, Mg arsenates, thus still suggesting the saturated pastes were undersaturated with respect to these metal arsenates (Table 2). The saturation indices coupled with direct SEM/EDAX observations (discussed later) suggest that discrete metal arsenate phases were not controlling aqueous As activities.

The PT sample and the lower pH RT sample (Soils

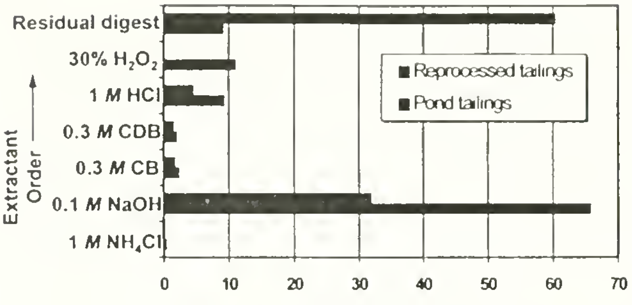

Fig. 1. Percentage of total As recovered from each sequential extractant for both the reprocessed tailings and pond tailings.

A and E, respectively, Table 2) were chosen for further sample characterization and column experiments because their low pH has apparently prevented natural revegetation in the field. Liming is therefore the likely remediation strategy (Neuman et al., 1993b). Sixty percent of As in the RT was found in the residual fraction (Fig. 1), with 32% of the remainder in the NaOH fraction (nonoccluded Fe/Al oxides; Olsen and Sommers, 1982). Conversely, only 9% of the As in the PT existed in the residual fraction, while 66% was found in the NaOH fraction. Although 0.1 *M* NaOH could also extract As bound as Fe or Al arsenates, the saturated paste data suggested that these materials were undersaturated with respect to these metal arsenate phases. The large difference in readily extractable As between these two samples suggests a significant difference in As lability. Arsenic in the PT sample may be considered more susceptible to mobilization compared to the RT, as will be discussed further.

Analysis of PT and RT using SEM-EDAX revealed no solid phases concentrated in As. Most particles contained As near or below the detection limit of the instrument (approximately 0.2% by atom), although some particles contained as much as 6% As. Particles containing high levels of Fe, S, or As were further analyzed for possible identification of primary or secondary minerals. The S/Fe ratios in both samples were generally well below elemental ratios for pyrite, and fell closer to expected ratios for jarosite (Table 3). Although some of the PT particles had S/Fe ratios near arsenopyrite, As/Fe ratios were all well below the 1:1 ratio found in either arsenopyrite (FeAsS) or scorodite ($FeAsO_4 \cdot 2H_2O$). It is difficult to invoke from EDAX analyses alone the presence of specific primary or secondary minerals of Fe, S, or As. The low S/Fe ratios in most of these samples (as compared to pyrite) suggest conservation of Fe (likely as Fe oxyhydroxides) relative to S. The formation of jarosite would not be unexpected in these samples, given that it is a common secondary mineral formed from the oxidation of pyrite (Dixon and Weed, 1977); however, we found no evidence for the presence of residual arsenopyrite or secondary formation of scorodite. It is likely, based on the strong affinity of As for Fe oxyhydroxides (Hingston et al., 1971; Goldberg, 1986; Fuller et al., 1993), that the majority of As was sorbed to these minerals.

Table 3. Molar ratios of S/Fe and As/Fe in particles of pond tailings and reprocessed tailings as determined by energy dispersive analysis of x-rays (EDAX). For comparison, ratios of S/Fe and As/Fe are shown for several possible mineral phases.

	Pond tailings		Reprocessed tailings	
Particle	S/Fe	As/Fe	S/Fe	As/Fe
1	0.05	0.11	0.52	0.01
2	0.89	0.13	0.25	0.02
3	0.67	0.04	0.18	0.02
4	1.80	0.36	0.53	0.02
5	0.35	0.11	0.16	0.03
6	1.15	0.08	0.12	0.03
7	1.04	0.07	0.40	0.04
8	0.93	0.48	0.31	0.05
Mean (SD)	0.86 (0.53)	0.17 (0.16)	0.31 (0.16)	0.03 (0.01)
Mineral				
Arsenopyrite	1	1	1	1
Pyrite	2	–	2	–
Jarosite	0.67	–	0.67	–
Scorodite	–	1	–	1

Column Experiments

Effluent As concentrations of the unlimed PT column reached steady-state levels near $10^{-6.5}$ *M* within several pore volumes (Fig. 2A). Liming the PT resulted in an effluent As concentration that was approximately two orders of magnitude higher than the unlimed column. After 13 pore volumes, effluent from the limed PT column peaked at approximately 10^{-4} *M*; 400-fold higher than in the unlimed column. The amount of As mobilized from the limed column during the experiment (26 pore volumes) represented 28% of the initial column As. Effluent pH values of the unlimed PT column were relatively stable at approximately 4.5 to 5 after several pore volumes. Liming resulted in an initial effluent pH near 8, followed by a gradual climb to pH values near 10.0. Increases in effluent pH of the limed column corresponded to increases in effluent As (Fig. 2A), consistent with the pH dependence of As sorption reactions on oxide minerals (Goldberg, 1986). Addition of 0.1 *M* $KHCO_3$ (pH 10.1) to the unlimed PT column at 23 pore volumes resulted in an increase in effluent pH and As; however, after three additional pore volumes, the hydraulic conductivity decreased to near 0, likely due to dispersion of colloidal material, and no further samples could be obtained.

Effluent As concentrations remained near $10^{-7.8}$ *M* at pH levels near 3.5 in the unlimed RT column for 100 pore volumes (Fig. 2B). The liming treatment resulted in an increase in effluent pH to values near 8 and effluent As to values near 10^{-7} *M*. Although the liming amendment increased effluent As concentrations by almost one order of magnitude in the RT sample, As concentrations ranged from two to three orders of magnitude lower than those found in the PT after liming. The total As content of the PT column was only 62 mg kg^{-1} (following dilution with SiO_2), compared with approximately 3400 mg kg^{-1} for the RT column. Therefore, the soluble/total As ratio was approximately 5000-fold higher in the limed PT column than in the RT column.

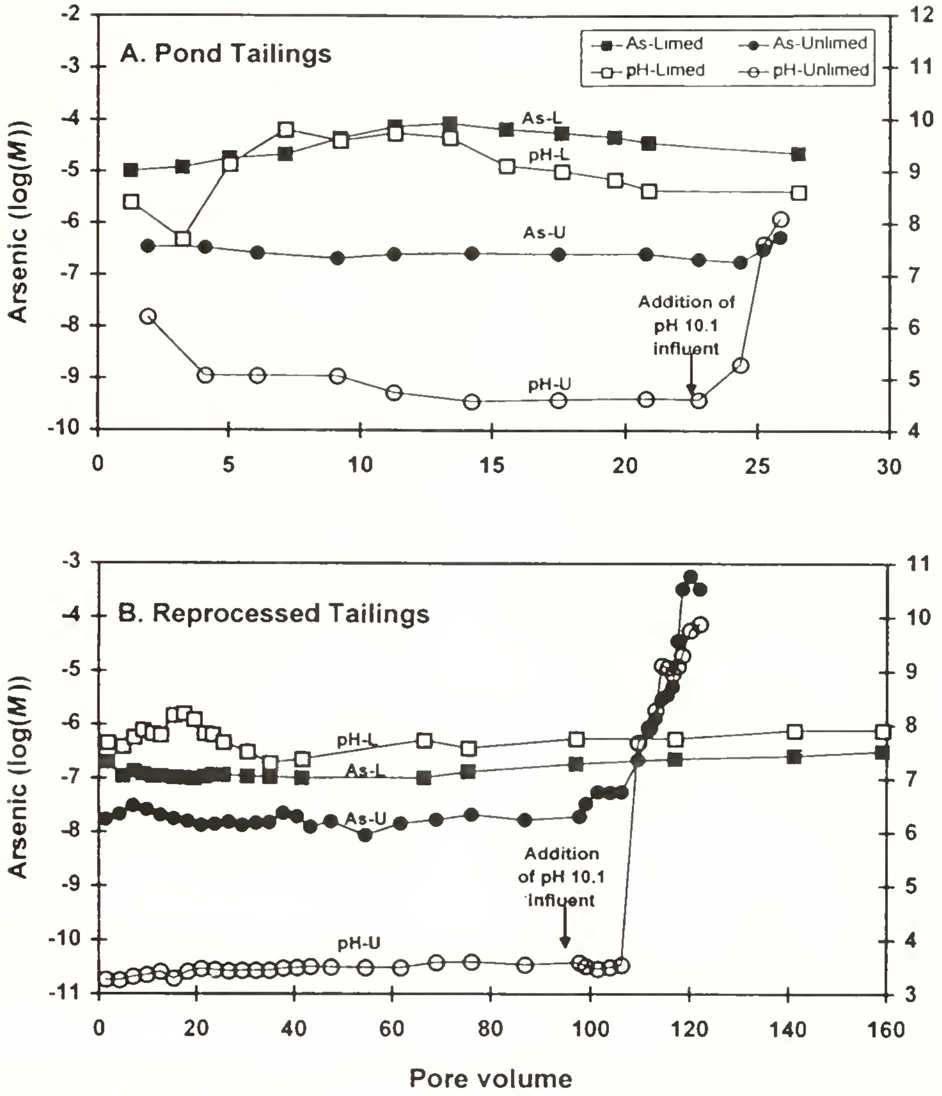

Fig. 2. Arsenic concentrations and pH levels in column effluent for limed and unlimed treatments of pond tailings (Fig. 2A) and reprocessed tailings (Fig. 2B). The arrow indicates the point of addition of 0.1 *M* $\mathrm{KHCO_3}$ (pH 10.1) influent to the unlimed column.

Differences in effluent As concentrations between the two limed samples were consistent with differences in the "lability" of bound As (Fig. 1). The NaOH-extractable As fraction is thought to represent As associated with Al or Fe and would likely be more susceptible to desorption with increases in pH following liming. Presumably, the large residual fraction in the RT (60%) would not be as "labile" after liming. Differences in As mobilization between the two samples may have also been influenced by differences in pH values after liming. Effluent pH values in the PT column reached 9.8 within 7 pore volumes and remained near 9 for almost 20 pore volumes. Conversely, pH values in the RT column remained near 8 for the majority of the column experiment. Based on the pH dependence of As sorption reactions on oxide minerals (Goldberg, 1986), higher pH values in the PT column likely contributed to more As desorption. In fact, when the pH of the unlimed RT column was raised to near 10, effluent As increased from approximately $10^{-7.8}$ to $10^{-3.2}$ *M* within 20 pore volumes. The fact that a high ionic strength/high pH influent solution (0.1 *M* $\mathrm{KHCO_3}$) was necessary to mobilize substantial amounts of As from the RT column is consistent with the higher residual As fraction in this sample. Results from the column experiments presented here are consistent with the pH dependence of surface complexation reactions of As on solid phase minerals such as goethite, ferrihydrite, gibbsite, Al hydroxides, and layer silicates.

Prior to liming, it was demonstrated that IAPs of PT and RT saturated paste extracts were undersaturated with respect to several metal arsenate solid phases (Table 2); however, after liming, changes in pore water chemistry necessitated a reanalysis of IAPs, especially considering the potential for Ca-arsenate to form in the presence of calcite (Sadiq et al., 1983). Solubility curves for both scorodite and Ca-arsenate were compared to selected effluent data for each of the three treatments (Fig. 3). All effluent solutions were found to be undersaturated with respect to these two solid phases. Although the possibility of an Fe-arsenate phase with lower solubility

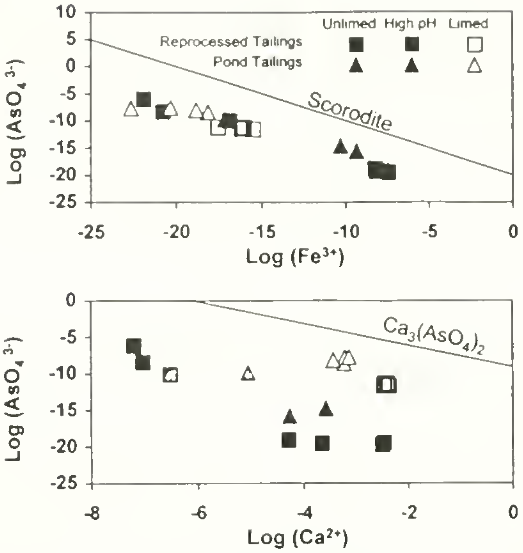

Fig. 3. Solubility diagrams for scorodite ($FeAsO_4 \cdot 2H_2O$) and $Ca_3(AsO_4)_2$ compared to activities of AsO_4^{3-}, Fe^{3+}, and Ca^{2+} in column effluent. Data points below the solubility lines indicate these solutions are undersaturated with respect to the given solid phase.

than that assumed for scorodite cannot be ruled out (Nordstrom and Parks, 1987), such phases have not been commonly observed in other studies. In addition, other possible solid phase Ca-arsenates such as $Ca(H_2AsO_4)_2$, $CaHAsO_4$, and $Ca_5H_2(AsO_4)_4$ can exist in a Ca-As-H_2O system. Each of these solid phases is more soluble than $Ca_3(AsO_4)_2$ (Nishimura et al., 1987), hence the effluent solutions were undersaturated with respect to these solid phases as well. These data, combined with the EDAX results, support the contention that the behavior of As after liming is not controlled by equilibrium with respect to solid phase arsenates, but is related to the pH dependence of As sorption reactions typically observed on oxide minerals.

CONCLUSIONS

Characterization of several representative mine tailing samples showed that soluble As levels were not correlated with total As, but were more strongly correlated with soil solution pH. Furthermore, saturated pastes of all mine tailing samples were undersaturated with respect to known metal arsenate solid phases. The mobility of As in two selected mine tailing samples was shown to increase substantially in unsaturated laboratory columns following a recommended liming treatment ($CaCO_3$/$Ca[OH]_2$). Adsorption-desorption reactions on oxide minerals are believed to be responsible for the pH dependence of soluble As concentrations, rather than precipitation-dissolution reactions of solid metal arsenates. The concentration of As in column effluent after liming was not correlated with total As in the two samples chosen for detailed column experiments. Sequential extractions showed substantial differences in "labile" As between the two samples, consistent with results from column experiments after liming. Consequently, the distribution of soil-bound As is important for determining the susceptibility of mine tailings to As mobilization following liming. In addition, the pH of the post-limed tailings is important for determining the amount of As mobilized after liming. Remediation of acidic mine tailings or other As-contaminated soils using lime amendments should be evaluated with respect to the potential effects on As mobilization, especially at contaminated sites hydraulically connected to surface or groundwaters.

REFERENCES

Dixon, J.B., and S.B. Weed (ed.) 1977. Minerals in soil environments. SSSA, Madison, WI.

Dove, P.M., and J.D. Rimstidt. 1985. The solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$. Am. Mineral. 70:838–844.

Fuller, C.C., J.A. Davis, and G.A. Waychunas. 1993. Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. Geochim. Acta. 57:2271–2282.

Ganje, T.J., and D.W. Rains. 1982. Arsenic. p. 385–402. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Gee, G.W., and J.W. Bauder. 1986. Particle size analysis. p. 383–411. *In* A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agron Monogr. 9. ASA and SSSA, Madison, WI.

Goldberg, S. 1986. Chemical modeling of arsenate adsorption on aluminum and iron oxide minerals. Soil Sci. Soc. Am. J. 50:1154–1157.

Goldberg, S., and R.A. Glaubig. 1988. Anion sorption on a calcareous, montmorillonitic soil-arsenic. Soil Sci. Soc. Am. J. 52:1297–1300.

Goldstein, J.I., D.E., Newbury, P. Echlin, D.C. Joy, A.D. Romig, Jr., C. Lyman, C. Fiori, and E. Lishin. 1992. Scanning electron microscopy and x-ray microanalysis. 2nd ed. Plenum Press, New York.

Hingston, F.J., A.M. Posner, and J.P. Quirk. 1971. Competitive adsorption of negatively charged ligands on oxides surfaces. p. 334–343. *In* F.C. Tompkins (ed.) Surface chemistry of oxides. Discussions of the Faraday Society, no. 52. The Faraday Soc., London.

Jacobs, L.W., J.K. Syers, and D.R. Keeney. 1970. Arsenic sorption by soils. Soil Sci. Soc. Am J. 34 750–754.

Johnston, S.E., and W.M. Barnard. 1979. Comparative effectiveness of fourteen solutions for extracting arsenic from four western New York soils. Soil Sci. Soc. Am J. 43:304–308.

Jones, A.A. 1982. X-ray fluorescence spectrometry. p. 85–121. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Neuman, D.R., F.F. Munshower, D.J. Dollhopf, Schafer and Associates, and CH2M Hill, Inc. 1993a. Silver Bow Creek RI/FS STARS Phase III, Final Summary Report, Vol I-IV, Montana State Univ., Bozeman.

Neuman, D.R., F.F. Munshower, and D.J. Dollhopf. 1993b. ARTS Phase I Final Report. Anaconda Revegetation Treatability Studies (ARTS). Anaconda Smelter Superfund Site. Document No. ASSS-Arts-1-FR-R1-102293. Montana State Univ., Bozeman.

Nishimura, T., C.T. Itoh, and K. Tozawa. 1987. Stabilities and solubilities of metal arsenites and arsenates in water and effect of sulfate and carbonate ions on their solubilities. p. 77–98. *In* R.G. Reddy et al. (ed.) Arsenic metallurgy, fundamentals and applications: Proceedings of a symposium. Metallurgical Society. Warrendale, PA.

Nordstrom, D.K., and H.M. May. 1989. Aqueous equilibrium data for mononuclear aluminum species. p. 29–53. *In* G. Sposito (ed.) The environmental chemistry of aluminum. CRC Press, Boca Raton, FL.

Nordstrom, D.K., and G.A. Parks. 1987. Solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$: Discussion. Am. Mineral. 72:849–851.

Nriagu, J.O. 1994. Arsenic in the environment. Vol. 26. Wiley Series in Advances in Environmental Science and Technology. John Wiley & Sons, New York.

Olsen, S.R., and L.E. Sommers. 1982. Phosphorus p. 403–430 *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Parker, D.L., L.W. Zelazny, and T.B. Kinraide. 1987. Improvements to the program GEOCHEM. Soil Sci. Soc. Am. J. 51:488–491.

Pontius, F.W., K.G. Brown, and C.-J. Chen. 1994. Health implications of arsenic in drinking water. J. AWWA 86(9):52–63.

Rhoades, J.H. 1982. Soluble Salts. p. 167–179. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Robins, R.G. 1981. The solubility of metal arsenates. Metallurgical Trans. B. The American Society for Metals and The Metallurgical Society of AIME. 12B:103–109.

Robins, R.G. 1987. Solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$: Discussion. Am. Mineral. 72:842–844.

Sadiq, M., and W.L. Lindsay. 1979. Selection of standard free energies of formation for use in soil chemistry. Tech. Bull. 134. Colorado State Univ. Exp. Stn., Fort Collins.

Sadiq, M., and W.L. Lindsay. 1981. Arsenic supplement to technical bulletin 134: Selection of standard free energies of formation for use in soil chemistry. Colorado State Univ. Exp. Stn., Fort Collins.

Sadiq, M., T.H. Zaidi, and A. A. Mian. 1983. Environmental behavior of arsenic in soils: Theoretical. Water, Air, Soil Pollut. 20:369–377.

Schafer, W., D.R. Neuman, F.F. Munshower, D.J. Dollhopf, and CH2M Hill, Inc. 1989. Final Summary Report-STARS Phase II: Field Scale Treatability Study Plot Construction. Reclamation Research Unit, Montana State Univ., Bozeman.

Sposito, G., and S.V. Mattigod. 1979. A computer program for the calculation of chemical equilibrium in soil solutions and other natural water systems. Kearney Foundation of Soil Sci. Univ. of California, Riverside.

Tessler, A., P.G.C. Campbell, and M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51(7):844–851.

Wagemann, R. 1977. Some theoretical aspects of stability and solubility of inorganic arsenic in the freshwater environment. Water Res. 12:139–145.

Welsch, E.P., J.G. Crock, and R. Sanzolone. 1990. Trace-level determination of arsenic and selenium using continuous-flow hydride generation atomic absorption spectrophotometry (HG-AAS). *In* B. Arbogast (ed.) Quality assurance manual for the branch of geochemistry, USGS: Open file Rep. 90-688.

Reprinted from the *Journal of Environmental Quality*
Volume 26, no. 4, July–August 1997, Copyright © 1997, ASA, CSSA, SSSA
677 South Segoe Rd., Madison, WI 53711 USA

Effects of pH and Phosphate Competition on the Transport of Arsenate

Jeffrey E. Darland and William P. Inskeep*

ABSTRACT

The effects of pH and phosphate (PO_4) competition on arsenate (AsO_4) sorption by soils and aquifer materials have been previously investigated in batch studies, however, little has been reported on processes that influence AsO_4 transport through porous media. Consequently, the objective of this study was to determine the effects of pH and PO_4 on the transport of AsO_4 under conditions where reaction and mass transfer rates may be controlling pore-water AsO_4 concentrations. Saturated column transport experiments (pore water velocity = 1 cm h^{-1}) were performed using a sand containing *free* Fe oxides in which a pulse of $^{73}AsO_4$ (133 μM) was applied in the presence of 0, 13.4, 134, and 1340 μM PO_4 at pH values of 4.5, 6.5, and 8.5. Breakthrough curves (BTCs) of AsO_4 exhibited low recovery and significant tailing at pH values of 4.5 and 6.5 in the absence of PO_4. Competition between PO_4 and AsO_4 for sorption sites resulted in increased AsO_4 mobility; however, even in the presence of PO_4 levels representing more than 100% of maximum sorption capacity for the columns, significant amounts of AsO_4 remained sorbed to the sand. Application of a continuous PO_4 pulse to a column containing sorbed AsO_4 resulted in an increase in AsO_4 recovery (>35%); however, even after total PO_4 loading exceeded the column capacity by more than two orders of magnitude, approximately 40% of the applied AsO_4 remained sorbed to the sand indicating that rates of AsO_4 desorption play an important role in transport of AsO_4 through porous media.

THE PH DEPENDENCE of AsO_4 adsorption has been investigated on numerous solid phases including amorphous Al hydroxide (Anderson et al., 1976), amorphous Fe hydroxide (Pierce and Moore, 1982), goethite and gibbsite (Goldberg, 1986; Hingston et al., 1971), kaolinite, montmorillonite, calcite, and quartz (Goldberg and Glaubig, 1988; Frost and Griffin, 1977; Xu et al., 1991). It is well established that adsorption of AsO_4 on Fe and Al hydroxides (including goethite and gibbsite) increases with decreasing pH to pH values near 3. Arsenate sorption on calcite and layer silicate minerals generally shows a maximum in the pH range of 4 to 6. Adsorption of AsO_4 onto clean, crystalline quartz was demonstrated to be negligible at pH values above 3 (Xu et al., 1991). The existing adsorption data show that in natural systems, AsO_4 is preferentially adsorbed to Fe and Al oxide minerals compared to kaolinite, montmorillonite, calcite, or quartz (Fordham and Norrish, 1979; Jacobs et al. 1970; Johnston and Barnard, 1979; Livesey and Huang, 1981).

Research has also shown substantial competition between AsO_4 and PO_4 sorption on a variety of soils and oxide minerals (Goldberg, 1986; Hingston et al., 1971; Peryea, 1991; Roy et al., 1986a,b). In soils that have been previously contaminated with lead AsO_4 pesticides, application of PO_4 fertilizers has been shown to result in increased As mobility (Peryea, 1991). Hingston et al. (1971) modeled the competition between AsO_4 and PO_4 on both goethite and gibbsite by a modified Langmuir isotherm using selectivity coefficients derived from experimental data involving binary mixtures over a wide range of concentrations. This approach has been extended to natural soils as well (Roy et al., 1986a,b). Goldberg (1986) successfully used a constant capacitance model to predict the competition between AsO_4 and PO_4 on gibbsite over a range of AsO_4 and PO_4 solution concentrations, with surface complexation constants determined from a binary system in which AsO_4 and PO_4 were present in equimolar amounts.

While there has been substantial research on the effects of pH and PO_4 competition on AsO_4 adsorption in batch studies, there is little data regarding the effects of these processes on transport of AsO_4 through porous media. Furthermore, while these processes have been quantified and modeled in batch systems, such systems typically are well mixed with high solution to solid ratios, and represent near equilibrium conditions. It is unclear the extent to which such data may be extrapolated to transport environments where reaction and mass transfer rates may be controlling pore water AsO_4 concentrations (Darland and Inskeep, 1997). Consequently, the objectives of this research were to determine the (i) effect of pH on AsO_4 transport through a representative sand, (ii) extent to which simultaneous competition between AsO_4 and PO_4 for adsorption sites affects AsO_4 transport, (iii) effect of pH on the competition between PO_4 and AsO_4 for adsorption sites during transport, and (iv) extent to which modification of pore water PO_4 concentration could increase AsO_4 mobility in contaminated aquifer sands. The focus of this study was to elucidate processes important in the transport of As under oxidizing conditions where As(V) is the predominant species. Appropriate mathematical expressions necessary for modeling the transport of As under column conditions are discussed in a separate study (Darland and Inskeep, 1997).

MATERIALS AND METHODS

Reagents and Analysis

Sand of mixed mineralogy (quartz, orthoclase, and plagioclase feldspars) was obtained from the Unimin Corporation (Emmett, ID), sieved to a particle-size range of 0.25 to 0.50 mm, acid washed three times with 0.05 M HCl, then rinsed with double deionized water (DD-H_2O) until the conductivity of the rinse had stabilized at <2 μS. The sand was then oven dried at 105°C, and characterized for surface area and chemical

---

J.E. Darland, Dep. of Environmental Science and Engineering, Oregon Graduate Institute of Science and Technology, Portland, OR 97291-1000; W.P. Inskeep, Dep. of Plant, Soil and Environmental Sciences, Montana State University, Bozeman, MT 59717. Journal Paper no. J-5013 of the Montana Agric. Exp. Stn., Bozeman, MT. Received 9 Apr. 1996. *Corresponding author (usswi@montana.edu).

Published in J. Environ. Qual. 26:1133–1139 (1997).

Abbreviations: BTCs, breakthrough curves; LS, liquid scintillation; IC, ion chromatography; AAM, ascorbic acid method; SA, surface area; CD, citrate-dithionite; EXAFS, Extended X-ray Absorption Fine Structure Spectroscopy; IAPs, ion activity products.

composition (Table 1). In addition, an acid purified quartz sand (SiO_2) was obtained (Fluka Chemical Co., Ronkonkoma, NY) presieved to a particle-size distribution of 0.074 to 0.42 mm and used in selected AsO_4 transport experiments. All chemical impurities in the purified quartz sand were below detection, as given by the manufacturer.

All AsO_4 solutions were prepared with the same source of analytical grade Na_2HAsO_4 salt, and diluted with DD-H_2O. Arsenate concentrations were measured by three different methods depending on the experiments performed. For the batch studies, AsO_4 was measured by atomic absorption with continuous hydride generation (HG-AAS). For the transport studies, radiolabeled $^{73}AsO_4$ (Los Alamos National Laboratory, Los Alamos, NM) was used in conjunction with liquid scintillation (LS) counting. Ion chromatography (IC) was used (Column = Dionex AS4A-SC; Eluant = 2.5 m*M* Na_2CO_3/2.66 m*M* $NaHCO_3$; Flowrate = 2 mL/min) periodically to verify concentrations determined by LS, and to verify that no reduction of arsenate to arsenite had occurred.

All PO_4 solutions were prepared with the same source of analytical grade K_2HPO_4 salt, and diluted with DD-H_2O. Phosphate concentrations were measured by two different methods depending on the experiments performed. For batch sorption studies, PO_4 was measured by the standard ascorbic acid method (AAM) (APHA, 1989). For transport studies, AsO_4 interference using the AAM necessitated the use of IC (Dionex AS4A-SC column) for PO_4 analysis.

Kinetic Adsorption Study

Separate batch studies were performed to evaluate the adsorption kinetics of AsO_4 and PO_4 onto the sand, and to determine an equilibrium time required for batch adsorption isotherm experiments. The batch kinetic adsorption experiments were performed in 15-mL polyethylene screw top bottles, and consisted of a 1:1 solid/solution ratio (5 g solid:5 mL solution), using initial concentrations of 150 μM AsO_4 and 360 μM PO_4. All solutions were prepared in a background of 0.01 *M* KCl. Samples were collected at time intervals of 2, 4, 8, 24, 48, 96, and 168 h, and were decanted and filtered through 0.45 μm nylon filters prior to analysis (AsO_4 by HG-AAS, PO_4 by AAM). Adsorbed concentrations were determined by difference between initial and final measured solute concentrations. Approximately 97% of the equilibrium adsorbed AsO_4 concentration was reached within 24 h. The PO_4 adsorption had only reached 92% of the equilibrium concentration within 24 h. Equilibrium (as defined by constancy of the ratio of adsorbed concentration to the concentration in solution) was not reached in both cases until at least 96 h.

Table 1. Physical and chemical characteristics of sand used in column transport experiments.

Element	Total content	
	g kg^{-1}†	stdev
Si	368	(5)‡
K	40	(4)
Al	38	(3)
Ca	5.7	(0.4)
Na	3.1	(0.9)
Fe	0.54	(0.25)
Mn	< 0.02	
P	< 0.02	
Fe–"Free"§	0.10	(0.01)
Al-"Free"	< 0.10	
Particle size:	0.25–0.50 mm	
Surface area:¶	390 ± 0.03 m^2 kg^{-1}	
CEC:#	2.7×10^{-3} mol$_c$ charge kg^{-1}	

† Total chemical composition by Li-metaborate fusion.
‡ Deviations represent standard deviations of three replicates.
§ Free Fe and Al oxides determined by citrate-dithionite extraction.
¶ Surface area determined using triple-point BET-N_2 isotherms.
# CEC = cation exchange capacity.

Batch Isotherms

Batch adsorption isotherms for AsO_4 onto the sand were performed at three initial PO_4 concentrations (0, 134, and 1340 μM) in 35-mL polypropylene centrifuge tubes, using a 1:1 solid/solution ratio (15 g solid:15 mL solution). Initial concentrations of 0, 1.3, 6.7, 13, 67, 133, and 266 μM AsO_4 were used at each initial PO_4 concentration. Samples were shaken for 96 h, and subsequently decanted and filtered through 0.45 μm nylon filters prior to analysis for AsO_4 by HG-AAS. Analysis of selected samples using IC indicated that, within the limits of detection, all of the total soluble As was present as AsO_4 species (i.e., As(V)). Adsorbed concentrations for AsO_4 were determined by difference between initial and final measured solute concentrations. Adsorption isotherms at each initial PO_4 concentration were fit to the Langmuir model using nonlinear regression according to the equation:

$$S = \Gamma_0 \frac{K_L \cdot C}{1 + K_L \cdot C}$$

where S is adsorbed concentration (μmol kg^{-1}), C is solution concentration (μmol L^{-1}), K_L is an empirical affinity parameter (L μmol^{-1}), and Γ_0 is maximum adsorption density (μmol kg^{-1}).

Column Transport Experiments

Column transport experiments were performed on the sand under saturated conditions at three different pH values (4.5, 6.5, and 8.5) for a single AsO_4 concentration (133 μM) in conjunction with four different PO_4 concentrations representing molar P/As ratios of 0, 0.1, 1.0, and 10. Transport experiments were performed using polycarbonate columns (2.8 cm diam, 8 cm length) containing 76.5 g sand, resulting in a bulk density of 1.55 g cm^{-3} and a calculated porosity of 0.41. The end caps of the column consisted of fine nylon mesh (<0.1 mm) supported by a Teflon plate drilled with 1-mm holes on 3-mm centers. A syringe pump (Soil Measurement Systems, Tucson, AZ) was used to provide flow to the columns.

Typical transport experiments were performed as follows. After initial saturation and conditioning with 0.01 *M* KCl to the desired pH, approximately one pore volume of ^3H_2O (~500 Bq mL^{-1}) in 0.01 *M* KCl was pulsed through the columns (direction of flow = bottom to top) at an average pore water velocity of 1 cm h^{-1} (8 h per pore volume; 0.25 mL pump volumes at a frequency of 350 s), followed by 0.01 *M* KCl. After complete recovery of the ^3H_2O pulse (~6 pore volumes total flow), one pore volume of a combined AsO_4/PO_4 solution (in 0.01 *M* KCl) was applied, followed by 0.01 *M* KCl. Four separate runs were performed at each pH value, keeping the AsO_4 concentration constant (133 μM; ~1650 Bq mL^{-1} ^{73}As), and varying the concentration of PO_4 (0, 13.4, 134, and 1340 μM). The experiments were continued for approximately 20 pore volumes (approximately 7 d) until the tailing of AsO_4 in columns effluent was well established and AsO_4 concentrations were near baseline levels.

The native pH of column effluent using unbuffered 0.01 *M* KCl was approximately 4.5. A carbonate-buffered eluant solution (pCO_2 = 0.0003 atm) in 0.01 *M* KCl was used to obtain constant column effluent pH values of 6.5 and 8.5. The buffered 0.01 *M* KCl solutions were prepared by pH adjustment with KOH under conditions of continuous sparging with air until the pH of the eluant solutions had stabilized. A separate column experiment was performed at pH = 8.5 under N_2 (g) to determine if the HCO_3^-/CO_3^{2-} concentrations in the CO_2(g) buffered pH 8.5 systems significantly affected the transport of AsO_4 via HCO_3^- or CO_3^{2-} competition. Effluent pH values were measured with an in-line pH electrode to prevent sample exposure to atmospheric CO_2 prior to pH measurement. The experimental protocol was identical to the previous columns, and used the same AsO_4 concentration (133 μM; ~1650 Bq mL^{-1} ^{73}As) in the absence of PO_4.

An additional column experiment was performed to assess the effect of PO_4 on AsO_4 desorption in a column already loaded with an AsO_4 pulse. The column was conditioned (0.01 M KCl) and loaded with a one pore volume pulse of 143 μM AsO_4 (~1650 Bq mL^{-1} ^{73}As) at a pH of 4.5. After 20 pore volumes, the 0.01 M KCl eluant was replaced with an eluant containing 1420 μM PO_4 (10:1 molar ratio of P/As) in 0.01 M KCl. The experiment was continued for an additional 15 pore volumes until sufficient As tailing had been established.

For comparison to the reactive sand used above, a transport study was also performed using acid purified quartz sand at an unbuffered pH of approximately 7.0. The column was conditioned with 0.01 M KCl, and loaded with a 1 pore volume pulse of a 133 μM AsO_4 solution and eluted according to the methods discussed previously. The experiment was continued until sufficient tailing had been established (~10 pore volumes), although AsO_4 recovery of >95% was observed in column effluent within five pore volumes.

All column effluent was passed through an in-line 0.45 μm nylon filter, then collected in glass test tubes using a fraction collector (approx. eight samples per pore volume). Effluent samples were analyzed for pH, followed by $^{73}AsO_4$ using LS. Ion chromatography was used to analyze PO_4 concentrations and to verify reduction of arsenate to arsenite had not occurred during transport. After termination, the sand from the columns was extracted with a mixture of 6 M HCl and 3 M HNO_3 to desorb the remaining adsorbed AsO_4, and the resulting extract analyzed for ^{73}As using LS to determine mass balance of applied $^{73}AsO_4$. In all cases, the total recovery of applied $^{73}AsO_4$ was >95%.

Determination of Column Transport Parameters

Individual sample volumes from the transport experiments were determined by the mass of the collected samples, and the water flux was determined as the average value of sample volume divided by the collection interval. Pore water velocity was then determined as the water flux divided by volumetric water content ($q\ \theta_V^{-1}$), as determined by the equation $\theta_V = 1 - (\rho/2.65)$ assuming a particle density of 2.65 g cm^{-3} and complete saturation in the columns, where ρ is the bulk density (g cm^{-3}). Relative concentration (C/C_o) was determined as the ratio of the collected ^3H_2O or AsO_4 concentration to the applied ^3H_2O or AsO_4 concentration in the pulse, and the number of pore volumes was determined as the ratio of cumulative collected volume to the liquid volume of a saturated column. Breakthrough curves for ^3H_2O were fit to the one-dimensional convection dispersion equation, with the computer program CXTFIT (Parker and van Genuchten, 1984), and were used to verify that no transport related nonequilibrium existed in any of the column runs. Dimensionless BTCs for AsO_4 were plotted using relative concentration (C/C_o) vs. pore volumes of the column outflow. Cumulative recovery of applied AsO_4 collected in the effluent is also presented on all BTCs.

RESULTS AND DISCUSSION

Batch Adsorption

The kinetics of AsO_4 and PO_4 adsorption onto the sand showed that at least 96 h was needed to reach equilibrium for both AsO_4 and PO_4 adsorption in a well-mixed batch system (Fig. 1). This is consistent with results from other studies showing a slow approach to equilibrium for AsO_4 adsorption onto amorphous Al hydroxides (Anderson et al., 1976) and ferrihydrite (Fuller et al., 1993). Similarly, PO_4 adsorption onto Fe and Al hydroxides has been shown to exhibit a slow approach to equilibrium (Bolan et al., 1985). Slow adsorption kinetics have been previously attributed to diffusion limitations within pore spaces of small aggregated particles in the case of PO_4 adsorption onto ferrihydrite (Willett et al., 1988). The actual chemical step in the adsorption process of AsO_4 and PO_4 onto Fe and Al oxides and clay minerals is quite rapid, generally on the order of milliseconds (Grossl and Sparks, 1995; Amacher, 1991; Sparks and Zhang, 1991). The slow approach to equilibrium observed in this experiment suggests that the kinetics of AsO_4 and PO_4 adsorption onto the sand were limited by mass transfer, such as film and/or interparticle diffusion. The sand used in the current study had a $N_2(g)$ surface area (SA) of 0.39 $m^2\ g^{-1}$ (Table 1), which is more than 50 times the estimated geometric surface area (spherical). The higher $N_2(g)$-SA indicates a large degree of surface roughness (Anbeek, 1992), suggesting that micropores existed on the sand particles.

Adsorption isotherms for AsO_4 onto the sand in the absence and presence of PO_4 exhibited distinct Langmuirian behavior (Fig. 2). The observed data were modeled by best fit Langmuir isotherms (nonlinear regression), yielding maximum site densities (Γ_0's) for AsO_4 of 168, 112, and 7 μmol kg^{-1} in the presence of 0, 134, and 1340 μM initial PO_4 (0, 1:1, 10:1 molar ratios), respectively. The presence of a 1:1 molar ratio of P/As resulted in a decrease in the maximum AsO_4 adsorption density of 33% compared to the 0 μM P treatment. In the presence of a 10:1 molar P/As ratio, maximum AsO_4 adsorption was reduced by 96%. The influence of PO_4 competition on AsO_4 adsorption by the sand (Fig. 2) is consistent with AsO_4/PO_4 competition reported in other studies (Hingston et al., 1971; Goldberg, 1986).

Previous studies on the adsorption of AsO_4 by Fe hydroxides have shown that the maximum adsorption density of AsO_4 onto ferrihydrite is an order of magnitude greater than onto goethite (Pierce and Moore,

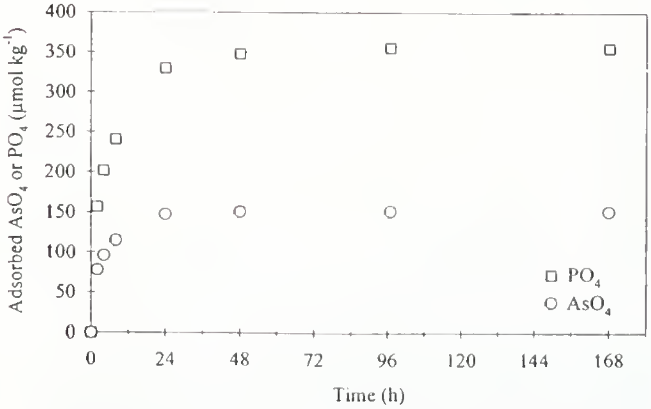

Fig. 1. Adsorption kinetics of arsenate (AsO_4) and phosphate (PO_4) onto sand (single ion experiments) at a 1:1 solid/solution ratio and at pH values ranging from 4 to 5 (AsO_4) and 4 to 5.7 (PO_4). Initial concentrations were 150 μM AsO_4 and 360 μM PO_4 in a background solution of 0.01 M KCl.

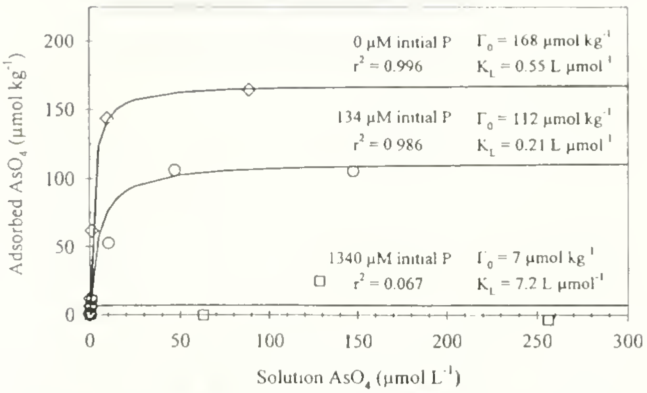

Fig. 2. Adsorption isotherms for arsenate (AsO_4) in the absence and presence of 134 µ*M* and 1340 µ*M* phosphate (PO_4) at a 1:1 solid/solution ratio and a pH range of 4 to 4.6 (all in 0.01 *M* KCl). Solid lines represent best-fit Langmuir isotherms, where Γ_0 = maximum adsorption density and K_L = empirical affinity parameter.

1982; Grossl and Sparks, 1995, Hingston et al., 1971). At a pH of 6, Pierce and Moore (1982) reported a maximum site density for ferrihydrite of 0.12 mol AsO_4/mol Fe, although no surface area was reported for the ferrihydrite samples used. At the same pH, Grossl and Sparks (1995) reported a maximum site density for goethite of 0.0084 mol AsO_4/mol Fe with a sample surface area of 50 m^2/g, while Hingston et al. (1971) reported a maximum site density for goethite of 0.012 mol AsO_4/mol Fe with a sample surface area of 60 m^2/g.

Results of the citrate-dithionite (CD) extraction indicated that the sand used in the current study contained 0.01% by weight *free* Fe, presumably as Fe oxides and hydroxides (Table 1). If it is assumed that AsO_4 adsorption by the sand was a result of coordination with surface sites on Fe oxides, a reasonable assumption given the strong preference of Fe oxides for AsO_4 compared to other soil phases (Fordham and Norrish, 1979; Jacobs et al. 1970; Johnston and Barnard, 1979; Livesey and Huang, 1981), then the maximum site density at pH 4.5 for the sand used in the current study was 0.095 mol AsO_4/mol *free* Fe. Pierce and Moore (1982) reported site densities on ferrihydrite of 0.16 and 0.12 mol AsO_4/mol Fe at pH values of 4 and 5, respectively, which is slightly greater than the calculated values for this experiment. However, Pierce and Moore (1982), used a batch-produced ferrihydrite in a well-mixed system, which would likely have a higher surface area than the *free* Fe oxides present on the sand grains used in the current study.

Effects of pH on Arsenic Transport

The transport of AsO_4 at pH values of 4.5 and 6.5 exhibited significant retardation, tailing and poor recovery of applied AsO_4 (Fig. 3). In contrast, the transport of AsO_4 at pH 8.5 was more rapid and resulted in a more symmetrical BTC (Fig. 3). After 10 pore volumes, the percent of applied AsO_4 recovered in the column effluent was 35.6, 39.2, and 100 for the columns at pH 4.5, 6.5, and 8.5, respectively. None of the predominant mineral phases present in the sand (quartz, feldspars) would be expected to sorb appreciable quantities of AsO_4. For comparison, the transport of AsO_4 through acid purified silica sand exhibited essentially no retardation or tailing with AsO_4 recovery in column effluent exceeding 95% within five pore volumes (Fig. 4). This is consistent with the minimal adsorption of AsO_4 onto quartz observed in batch studies at pH values >3 (Xu et al., 1991). The calculated sorbed AsO_4 site densities per mole *free* Fe (from AsO_4 sorption maxima) were similar to site densities obtained for Fe oxides in other studies, suggesting that the *free* Fe oxides present in the sand were responsible for the retardation and slow desorption of AsO_4 during transport at pH 4.5 and 6.5.

The enhanced transport of AsO_4 at pH 8.5 is consistent with the pH dependence of surface complexation reactions describing the adsorption of AsO_4 by metal oxide surfaces, where sorption of AsO_4 decreases dramatically at pH values >8 (Xu et al., 1991; Anderson et al., 1976; Pierce and Moore, 1982). Arsenate adsorption by Fe hydroxides can be categorized as a *ligand exchange* mechanism, and it has been shown by Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) that AsO_4 forms a combination of mono- and bidentate complexes with surface Fe sites (Waychunas et al., 1993). For AsO_4 adsorption onto goethite, these

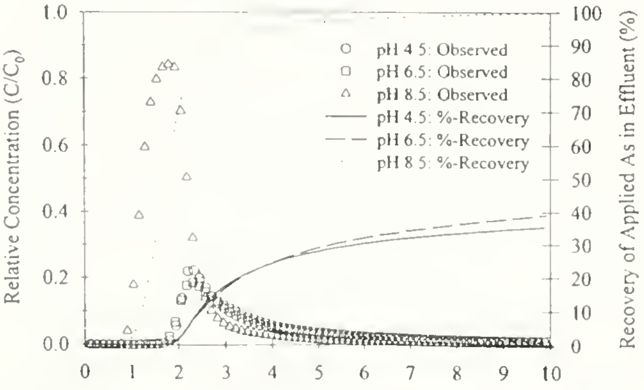

Fig. 3. Transport of arsenate (AsO_4) through a sand at three different carbon dioxide (CO_2) buffered pH values: 4.5, 6.5, and 8.5 (Column conditions: Pore water velocity = 1 cm h^{-1}; background solution = 0.01 *M* KCl; AsO_4 pulse = 1 pore volume at 133 µ*M*).

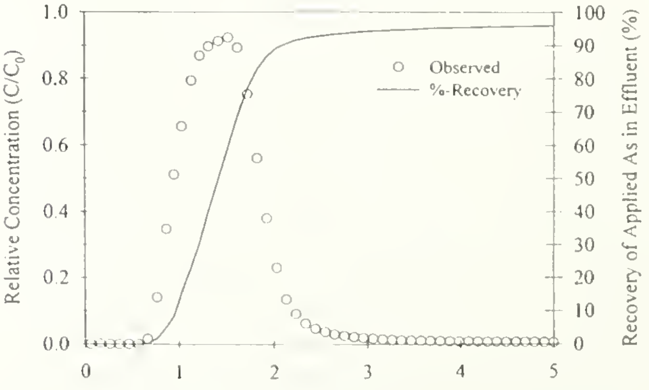

Fig. 4. Transport of arsenate (AsO_4) through clean quartz sand (Fluka Chemical Co.) at pH 7 (Column conditions: Pore water velocity = 1 cm h^{-1}; background solution = 0.01 *M* KCl; AsO_4 pulse = 1 pore volume at 133 µ*M*).

ligand exchange reactions have been represented by (Goldberg, 1986; Grossl and Sparks, 1995):

$$FeOH(s) + H_3AsO_4(aq) = FeH_2AsO_4(s) + H_2O$$

$$FeOH(s) + H_3AsO_4(aq) = FeHAsO_4^-(s) + H_2O + H^+(aq)$$

$$FeOH(s) + H_3AsO_4(aq) = FeAsO_4^{2-}(s) + H_2O + 2H^+(aq)$$

$$2FeOH(s) + H_3AsO_4(aq) = Fe_2HAsO_4(s) + 2H_2O$$

$$2FeOH(s) + H_3AsO_4(aq) = Fe_2AsO_4^-(s) + 2H_2O + H^+(aq)$$

The pH dependence of AsO_4 sorption predicted from these reactions as described by Goldberg (1986) and Grossl and Sparks (1995) supports the enhanced transport at pH 8.5 observed in this study.

The sorption and subsequent transport behavior of AsO_4 as a function of pH is dependent both on the surface charge of the sorptive phase and on the aqueous speciation of AsO_4. Zero points of charge (pH_{ZPC}) for amorphous $Fe(OH)_3$ (ferrihydrite) and a-FeOOH (goethite) range from 8.5 to 7.8 (Stumm and Morgan, 1981). It is expected that the pH_{ZPC} for the *free* Fe oxide present in the sand would fall in this range; consequently, we would expect that Fe-oxide surfaces were predominantly positively charged at pH values of 4.5 and 6.5 and predominantly negatively charged at a pH of 8.5. The predominant AsO_4 species at pH values of 4.5 and 6.5 is $H_2AsO_4^-$, and at a pH of 8.5, the predominant species is $HAsO_4^{2-}$. Consequently, at a pH of 8.5 the combination of a predominantly negative surface and a more negative AsO_4 solution species resulted in a dramatic increase in the mobility of AsO_4 (Fig. 3).

Effects of Carbonate Species

To test the effects of HCO_3^-/CO_3^{2-} ions (present in the $CO_2(g)$ buffered systems) on the transport of AsO_4 at pH 8.5, column experiments were performed in both $CO_2(g)$ buffered and $N_2(g)$ atmospheres (Fig. 5). Effluent samples from both systems were periodically analyzed for total alkalinity yielding average values for carbonate concentrations of 1.2 m*M* and <0.1 m*M* in $CO_2(g)$ and $N_2(g)$ systems, respectively. A value of 1.2 m*M* HCO_3^- is consistent with equilibrium of $\rho CO_2(g)$ = 0.0003 atm at pH 8.5.

After 10 pore volumes of elution, the percent of applied AsO_4 recovered in the column effluent was 100% in the presence of $CO_2(g)$, and >95% in the $N_2(g)$ system. While a majority (~90%) of the applied AsO_4 was eluted within three pore volumes, tailing was still observed in both columns (Fig. 5). The transport of AsO_4 in the $CO_2(g)$ buffered system exhibited a slight increase in recovery after three pore volumes, indicating that some competition of HCO_3^-/CO_3^{2-} for AsO_4 adsorption sites may have occurred during transport. However, results from this comparison confirm that enhanced transport of AsO_4 at pH 8.5 (Fig. 3) was caused primarily by increases in pH and not due to competition from HCO_3^-/CO_3^{2-} ions.

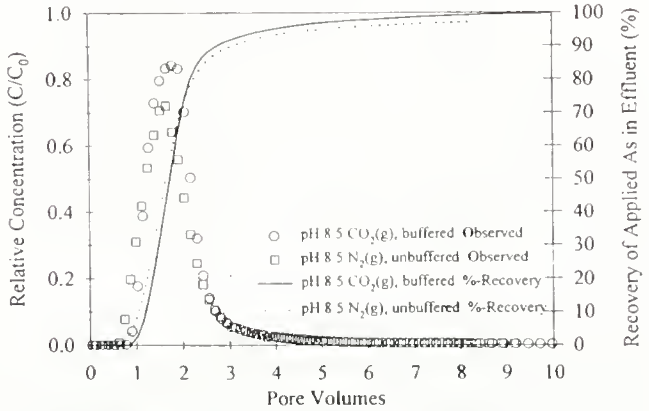

Fig. 5. Transport of arsenate (AsO_4) through sand at pH 8.5 in the presence of $CO_2(g)$ or $N_2(g)$ (Column conditions: Pore water velocity = 1 cm h^{-1}; background solution = 0.01 *M* KCl; AsO_4 pulse = 1 pore volume at 133 µ*M*).

Effects of Phosphate Competition on Arsenic Transport

At pH 4.5, increasing additions of PO_4 to column influent resulted in increased recoveries of applied AsO_4 and caused the AsO_4 BTCs to shift to the left, indicating a decrease in AsO_4 retardation (Fig. 6). These results are consistent with other studies showing enhanced mobility of AsO_4 in the presence of PO_4 (Peryea, 1991). After 10 pore volumes of elution, the percent of applied AsO_4 recovered in the column effluent was 35.6, 36.7, 63.5, and 88.4 for PO_4 concentrations of 0, 13.4, 134, and 1340 µ*M*, respectively. With the addition of 1340 µ*M* PO_4, the AsO_4 BTC occurred slightly after one pore volume, and had a peak concentration (C/C_0) near 1.2.

Breakthrough curves of AsO_4 in the presence of varying PO_4 concentrations at pH 6.5 (Fig. 7) exhibited the same general behavior as AsO_4 BTCs at pH 4.5, but in all cases the recovery of applied AsO_4 was greater at pH 6.5 than at pH 4.5, consistent with the effects of pH noted in Fig. 3. After 10 pore volumes of elution, the percent of applied AsO_4 recovered in the column efflu-

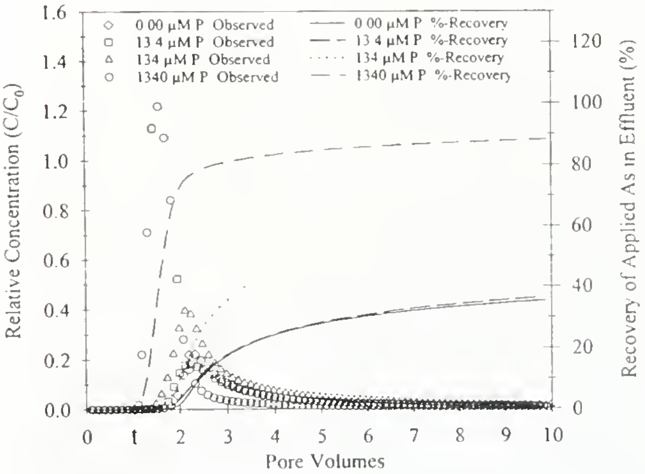

Fig. 6. Transport of arsenate (AsO_4) through sand at pH 4.5 in the presence of 0, 13.4, 134, and 1340 µ*M* PO_4 (Column conditions: Pore water velocity = 1 cm h^{-1}; background solution = 0.01 *M* KCl; AsO_4 pulse = 1 pore volume at 133 µ*M*).

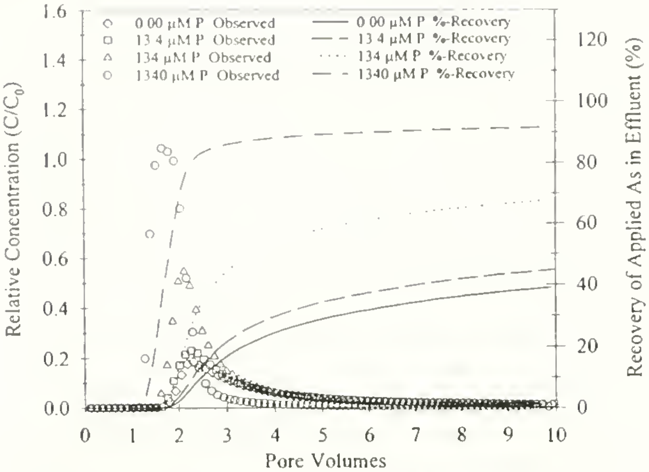

Fig. 7. Transport of arsenate (AsO_4) through sand at pH 6.5 (CO_2 buffered) in the presence of 0, 13.4, 134, and 1340 μ*M* PO_4 (Column conditions: Pore water velocity = 1 cm h^{-1}; background solution = 0.01 *M* KCl; AsO_4 pulse = 1 pore volume at 133 μ*M*).

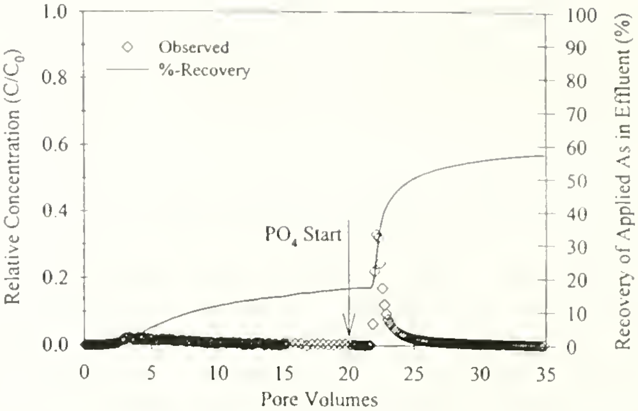

Fig. 8. Transport of arsenate (AsO_4) through sand at pH 4.5 followed by continuous addition of 1420 μ*M* PO_4 at 20 pore volumes (Column conditions: Pore water velocity = 1 cm h^{-1}; background solution = 0.01 *M* KCl; AsO_4 pulse = 1 pore volume at 143 μ*M*).

ent was 39.2, 45.0, 67.9, and 91.6 for the columns at PO_4 concentrations of 0, 13.4, 134, and 1340 μ*M*, respectively. Again, with the addition of 1340 μ*M* PO_4, the AsO_4 BTC occurred slightly after one pore volume, and had a $C/C_0 > 1$.

The observation that relative C/C_0 were >1 for AsO_4 BTCs at pH 4.5 and 6.5 in the presence of 1340 μ*M* PO_4, indicates that AsO_4 was concentrated at the leading edge of the PO_4 BTC. Measurement of PO_4 concentration in the column effluent by IC verified that PO_4 breakthrough occurred immediately after AsO_4. While recovery of applied AsO_4 was dramatically enhanced by the addition of 1340 μ*M* PO_4 to the applied pulse, the recovery of applied AsO_4 still did not exceed 92%. This may indicate that certain sorption sites on the sand were specific for AsO_4, or that desorption of AsO_4 remained kinetically limited even in the presence of high concentrations of PO_4.

The total adsorption capacity of a column at pH 4.5 was estimated from the batch isotherm data as being 13.0 μmol (As or P) per packed column of sand. In a one pore volume pulse, the total input of AsO_4 was 2.7 μmol As, and the total input of PO_4 at molar P/As ratios of 0, 1:10, 1:1, and 10:1 was 0, 0.27, 2.7, and 27 μmol P, respectively. Consequently, the resulting total column loading (AsO_4 plus PO_4) for column experiments was 2.7, 3.0, 5.4, and 29.7 μmol per pulse at molar P/As ratios of 0, 1:10, 1:1, and 10:1, respectively. At a 10:1 molar P/As ratio, the total column adsorption capacity was exceeded by approximately 100%, indicating that there should have been sufficient PO_4 present in the column to compete for all adsorption sites.

An additional experiment was performed at pH 4.5 to evaluate the effects of PO_4 competition on AsO_4 transport after the applied AsO_4 had time (20 pore volumes ≈ 7 d) to react with the solid phase (Fig. 8). The recovery of AsO_4 from a one pore volume pulse of 143 μ*M* AsO_4 solution was only 20% following 20 pore volumes of 0.01 *M* KCl. At 20 pore volumes, a 1420 μ*M* PO_4 solution (10:1 P/As molar ratio with respect to the AsO_4 pulse) was applied as a continuous pulse. Arsenate recovery increased dramatically by more than 35% within 15 additional pore volumes of elution, however significant AsO_4 tailing was observed after the first five pore volumes of PO_4 addition, indicating that a large fraction of the adsorbed AsO_4 was not readily desorbed, even in the presence of excess PO_4. Furthermore, the percent recovery of applied AsO_4 in the effluent was <60% after 15 pore volumes of PO_4 elution and 35 pore volumes total elution. In contrast, a simultaneously applied PO_4 pulse resulted in a recovery of >85% within 10 pore volumes (Fig. 6). This suggests a decrease in AsO_4 desorption rates in 'aged' columns compared to columns receiving simultaneous inputs of PO_4 and AsO_4.

It is unclear whether the difference in AsO_4 recovery (in the presence of PO_4) between 'aged' and 'unaged' systems was due to changes in the apparent desorption rates of surface Fe-As complexes, the formation of As precipitates, or the formation of occluded Fe-As surface complexes. Although no studies were performed to identify possible AsO_4 solid phase formation, calculations of ion activity products (IAPs) suggest that our solutions were well undersaturated with respect to AsO_4 solid phases. Furthermore, Waychunas et al. (1993) convincingly showed that scorodite ($FeAsO_4 \cdot 2H_2O$) formation on ferrihydrite was not important even at AsO_4 concentrations of 5 m*M*. Consequently, it is likely that the observed decrease in AsO_4 recovery in the 'aged' system was due to a decrease in the apparent desorption rates of surface-bound As. In 'aged' systems, sufficient time may exist for AsO_4 to diffuse further into the sorbing matrix, resulting in apparent decreases in As desorption rates, even in the presence of high PO_4 concentrations.

In a separate study, Darland and Inskeep (1997) demonstrated that the transport of AsO_4 (pH = 4.5) through this sand exhibited chemical nonequilibrium at pore water velocities ranging from 0.2 to 90 cm h^{-1}. These velocities exceeded time scales necessary for sorption-desorption equilibrium. The tailing in AsO_4 BTCs observed in this study in the presence and absence of PO_4

also reflect the effects of slow adsorption-desorption kinetics relative to pore water velocity. For example, at slower pore water velocities (<0.2 cm h^{-1}), As recovery from the aged column may have more closely approximated equilibrium conditions, resulting in a greater recovery of applied As. Consequently, the effects of As-P sorption competition on AsO_4 transport observed in this study cannot necessarily be modeled using sorption equilibria for AsO_4 and PO_4, but would require kinetic approaches relying on formulation of empirical (or fundamental) kinetic expressions describing AsO_4 and PO_4 sorption-desorption (Darland and Inskeep, 1997).

CONCLUSIONS

Batch adsorption experiments and column transport experiments indicated that AsO_4 was strongly sorbed to a sand containing minor amounts of *free* Fe oxides (0.01% Fe, w/w). Given that the primary constituents present in the sand (feldspar and quartz) are not considered strong sorptive phases for AsO_4, the *free* Fe oxides present (as determined using citrate-dithionite selective dissolution) were likely the principal reactive phases for AsO_4 sorption. Furthermore, the maximum adsorption density of 0.095 mol AsO_4 per mol *free* Fe determined from batch adsorption isotherms is consistent with values reported for pure Fe-oxide systems. At a pH above the expected pH_{ZPC} of the Fe-oxyhydroxide phase (i.e., pH 8.0), AsO_4 transport through the aquifer sand increased dramatically, where AsO_4 recovery exceeded 95% within 10 pore volumes. The effects of pH on the transport of AsO_4 appear consistent with the pH dependence of surface complexation reactions describing AsO_4 sorption by oxide minerals.

Phosphate was shown to effectively compete with AsO_4 for adsorption sites on the sand in batch isotherms as well as in saturated transport studies. The PO_4 competition, however, was not sufficient to desorb all of the applied AsO_4 either in simultaneously applied pulses, or in a column where AsO_4 was applied prior to a concentrated PO_4 pulse. When the applied PO_4 exceeded the calculated column adsorption capacity by twofold, some AsO_4 remained adsorbed onto the sand. Likewise, when a high concentration of PO_4 (1420 μM) was continuously applied to a column that had been previously spiked with an AsO_4 pulse, recovery of AsO_4 in the column effluent did not exceed 60%, even though the total PO_4 loading was greater than the calculated column capacity by more than two orders of magnitude. These results suggest that AsO_4 desorption kinetics may play an important role in the transport of AsO_4 through porous media.

ACKNOWLEDGMENTS

This research was supported by the Montana Water Resources Center, the Montana Agricultural Experiment Station, and the Montana Department of Natural Resources and Conservation. We appreciate the assistance of Mr. Clain Jones and Dr. Hesham Gaber.

REFERENCES

Amacher, M.C. 1991. Methods of obtaining and analyzing kinetic data. p. 19–59. *In* D.L. Sparks and D.L. Suarez (ed.) Rates of soil chemical processes. SSSA Spec. Publ. 27. SSSA, Madison, WI.

American Public Health Association 1989. Ascorbic acid method. p. 409–425. *In* Standard methods for the examination of water and wastewater. APHA, New York.

Anbeek, C. 1992. Surface roughness of minerals and implications for dissolution studies. Geochim. Cosmochim. Acta 56:1461–1469.

Anderson, M.A., J.A. Ferguson, and J. Gavis. 1976. Arsenate adsorption on amorphous aluminum hydroxide. J. Colloid Interface Sci. 54:391–399.

Bolan, N.S., N.J. Barrow, and A.M. Posner. 1985. Describing the effect of time on sorption of phosphate by iron and aluminum hydroxides. J. Soil Sci. 36:187–197.

Darland, J.E., and W.P. Inskeep. 1997. Effects of pore water velocity on the transport of arsenate. Environ. Sci. Technol. 31:704–709.

Fordham, A.W., and K. Norrish. 1979. Arsenate-73 uptake by components of several acidic soils and its implications for phosphate retention. Aust. J. Soil Res. 17:307–316.

Frost, R.R., and R.A. Griffin. 1977. Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals. Soil Sci. Soc. Am. J. 41:53–57.

Fuller, C.C., J.A. Davis, and G.A. Waychunas. 1993. Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. Geochim. Cosmochim. Acta 57:2271–2282.

Goldberg, S. 1986. Chemical modeling of arsenate adsorption on aluminum and iron oxide minerals. Soil Sci. Soc. Am. J. 50:1154–1157.

Goldberg, S., and R.A. Glaubig. 1988. Anion sorption on a calcareous, montmorillonitic soil-arsenic. Soil Sci. Soc. Am. J. 52:1297–1300.

Grossl, P.R., and D.L. Sparks. 1995. Evaluation of contaminant ion adsorption/desorption on goethite using pressure-jump relaxation kinetics. Geoderma 67:87–101.

Hingston, F.J., A.M. Posner, and J.P. Quirk. 1971. Competitive adsorption of negatively charged ligands on oxide surfaces. Discuss. Faraday Soc. 52:334–342.

Jacobs, L.W., J.K. Syers, and D.R. Keeney. 1970. Arsenic sorption by soils. Soil Sci. Soc. Am. J. 34:750–754.

Johnston, S.E., and W.M. Barnard. 1979. Comparative effectiveness of fourteen solutions for extracting arsenic from four western New York soils. Soil Sci. Soc. Am. J. 43:304–308.

Livesey, N.T., and P.M. Huang. 1981. Adsorption of arsenate by soils and its relation to selected chemical properties. Soil Sci. 131:88–94.

Parker, J.C., and M. Th. van Genuchten. 1984. Determining transport parameters from laboratory and field tracer experiments. Virginia Agric. Exp. Stn. Bull. 84-3.

Peryea, F.J. 1991. Phosphate-induced release of arsenic from soils contaminated with lead arsenate. Soil Sci. Soc. Am. J. 55:1301–1306.

Pierce, M.L., and C.B. Moore. 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Res. 16:1247–1253.

Roy, W.R., J.J. Hassett, and R.A. Griffin. 1986a. Competitive coefficients for the adsorption of arsenate, molybdate, and phosphate mixtures by soils. Soil Sci. Soc. Am. J. 50:1176–1182.

Roy, W.R., J.J. Hassett, and R.A. Griffin. 1986b. Competitive interactions of phosphate and molybdate on arsenate adsorption. Soil Sci. 142:203–210.

Sparks, D.L., and P.C. Zhang. 1991. Relaxation methods for studying kinetics of soil chemical phenomena. p. 61–94. *In* D.L. Sparks and D.L. Suarez (ed.) Rates of soil chemical processes. SSSA Spec. Publ. 27. SSSA, Madison, WI.

Stumm, W., and J.J. Morgan. 1981. Aquatic chemistry and introduction emphasizing chemical equilibria in natural waters. John Wiley & Sons, New York.

Waychunas, G.A., B.A. Rea, C.C. Fuller, and J.A. Davis. 1993. Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. Geochim. Cosmochim. Acta 57:2251–2269.

Willett, I.R., C.J. Chartres, and T.T. Nguyen. 1988. Migration of phosphate into aggregated particles of ferrihydrite. J. Soil Sci. 39:275–282.

Xu, H., B. Allard, and A. Grimvall. 1991. Effects of acidification and natural organic materials on the mobility of arsenic in the environment. Water Air Soil Pollut. 57:269–278.

Reprinted from the *Journal of Environmental Quality*
Volume 28, no. 4, July–Aug. 1999. Copyright © 1999, ASA, CSSA, SSSA
677 South Segoe Rd , Madison, WI 53711 USA

Arsenic Solubility and Attenuation in Soils of the Madison River Basin, Montana: Impacts of Long-Term Irrigation

C. A. Jones, W. P. Inskeep,* J. W. Bauder, and K. E. Keith

ABSTRACT

Arsenic concentrations in 850 km of the Madison and Upper Missouri Rivers exceed the Montana State human health standard (0.24 μM). In addition, ground water As concentrations in the northern portion of the Lower Madison River Valley are above the federal drinking water standard (0.67 μM) and correlate with high soluble As levels in overlying soils. The objectives of this study were to determine processes affecting As solubility in soils of the Madison and Upper Missouri River Basins and assess potential impacts of long-term irrigation with As-rich river water on As mobility. Sixteen irrigated (>20 yr of irrigation) and nonirrigated (never irrigated) soils were sampled in four major regions adjacent to the Madison and Upper Missouri Rivers. There were no significant differences ($\alpha = 0.05$) in total or soluble As levels between irrigated and nonirrigated soils within any of the four regions. In addition, sorption coefficients (K_d values) in six paired soils selected for additional chemical characterization were not significantly different ($\alpha = 0.05$) between irrigated and nonirrigated soils. Ammonium oxalate extractable Fe and Mn concentrations were found to be positively correlated with K_d, and Olsen P concentration was found to be negatively correlated with K_d based on a multiple linear regression ($r^2 = 0.92$). Sequential extractions performed for a subset of soils showed that labile As concentrations were similar between irrigated and nonirrigated soils. Soils that had been irrigated for >100 yr had additional As sorption capacities of at least 3 mg kg^{-1} in saturated column studies following 30 yr of simulated irrigation. Based on this suite of data, it was determined that irrigation history has not significantly affected As solubility or attenuation capacities in soils of the study area.

Geothermal discharge in Yellowstone National Park provides a continual source of As to the Madison and Missouri River system (Stauffer and Thompson, 1984; Nimick et al., 1998). Concentrations of As in 850 km of the Madison–Missouri mainstem (Fig. 1) exceed the Montana human health standard of 0.24 μM, with concentrations approaching 5 μM in the Madison River headwaters (Nimick et al., 1998). In addition, As levels exceed the USEPA drinking water standard of 0.67 μM in approximately 70 km^2 of ground water in the Lower Madison River Valley (Nimick, 1998) and As in saturated paste extracts from soils overlying this area range up to approximately 130 μM (Keith, 1995). A previous study suggested that evapoconcentration of applied irrigation water was increasing As concentrations in soils, ground water, and irrigation return flows of the Lower Madison River Valley (Sonderegger and Ohguchi, 1988). Based on this theory, Montana implemented controls in 1992 to prevent new irrigation projects that would raise As concentrations in downstream waters. To predict the effects of current and future irrigation projects in the Madison–Missouri River Basin, it is necessary to understand processes controlling As transport in both irrigated and nonirrigated soils.

Solubility of As in soils can be controlled by sorption–desorption, precipitation–dissolution, and oxidation–reduction reactions. Sorption of arsenate (As(V)), the thermodynamically favored species in oxidized environments, has been found to decrease with increased pH (Goldberg and Glaubig, 1988; Darland and Inskeep, 1997a; Jones et al., 1997; Raven et al., 1998). Surface complexation of As(V) at Fe oxide surfaces occurs primarily as a bidentate innersphere surface complex, although monodentate surface complexes are also possible based on x-ray absorption fine structure spectroscopy (Waychunas et al., 1995). Phosphate additions have been shown to substantially mobilize As(V) (Davenport and Peryea, 1991; Peryea, 1991; Darland and Inskeep, 1997a) due to competition for binding sites at the oxide surface. At low redox potentials (<20 mV at pH 7), arsenite (As(III)) is the thermodynamically stable species. Many studies have demonstrated that As(III) does not sorb as strongly as As(V) (Frost and Griffin, 1977; Pierce and Moore, 1982; Xu et al., 1991), and total soluble As concentrations often increase with decreased redox potential (Masscheleyn et al., 1991a; McGeehan and Naylor, 1994). Precipitation–dissolution reactions involving As are often less important than sorption–desorption reactions in surface soils because As(V) solid phases are generally too soluble to control equilibrium As(V) concentrations (Robins, 1981; Sadiq et al., 1983; Dove and Rimstidt, 1985; Nishimura et al., 1987). Conversely, As(III)-sulfide solid phases, such as amorphous As_2S_3 and orpiment, are stable in highly reduced systems (Webster, 1990; Eary, 1992) and may control As solubility in saturated soils and sediments.

Irrigation with Madison River water, containing approximately 0.6 to 1.3 μM of As (Nimick, 1998) has the potential to alter soil solution As concentrations through a variety of mechanisms. For example, sorbed As concentrations may increase due to irrigation, thereby supporting higher equilibrium solution As concentrations. Increased pore water velocities from irrigation also may affect solution As concentrations due to

---

C.A. Jones, W.P. Inskeep, and J.W. Bauder, Dep. of Land Resources and Environmental Sciences, Montana State Univ., Bozeman, MT 59717; and K.E. Keith, Univ. of Idaho, Caldwell, ID 83605. Contribution of the Montana Agric. Exp. Stn. Received 24 Aug. 1998. *Corresponding author (binskeep@montana.edu).

Published in J. Environ. Qual. 28:1314–1320 (1999).

Abbreviations: AAS, atomic absorption spectrophotometry; HGAAS, hydride generation atomic absorption spectrophotometry; AOE, ammonium oxalate extractable; I, irrigated; NI, nonirrigated; ICP-AES, inductively coupled plasma-atomic emission spectroscopy; RSD, relative standard deviation; IAP, ion activity product; SEM, scanning electron microscope; EDAX, energy dispersive analysis of x-rays; LMadN, lower Madison north; UMad, upper Madison; LMadS, lower Madison south; UMis, Upper Missouri; PWV, pore water velocity.

BLANK PAGE

kinetic limitations of As sorption. Darland and Inskeep (1997b) found that nonequilibrium conditions existed at pore water velocities as low as 0.2 cm h^{-1} in As transport studies; therefore, sorption equilibrium may not be achieved during irrigation events. Finally, flood irrigation may decrease redox potentials, favoring the formation of As(III), and possibly decreasing As sorption. In summary, irrigation could have a variety of effects on As solubility depending on specific site characteristics. Consequently, the objectives of the present study were to: (i) determine effects of long-term irrigation on accumulation of soil profile As, (ii) identify soil characteristics that control As sorption, (iii) compare As lability between irrigated and nonirrigated soils, and (iv) determine the potential for continued As attenuation in soils of the Madison and Upper Missouri River Basins.

MATERIALS AND METHODS

Sample Collection

Soil samples were collected during 1993 and 1994 at 16 paired (irrigated and nonirrigated) sites adjacent to the Madison and Missouri Rivers, Montana (Keith, 1995). Sampling sites were grouped into four major regions (Fig. 1): Upper Madison (Sites A1-A4), Lower Madison South (Sites B1-B4), Lower Madison North (Sites C1-C4), and Upper Missouri (Sites D1-D4). Sampling was concentrated in the Lower Madison because ground water in this vicinity has elevated As concentrations (0.25–2.3 μM; Nimick, 1998). Irrigated (I) soils had been irrigated with river water for >20 yr, and at least two soils (B1-I and C2-I) had been irrigated for approximately 110 yr. Nonirrigated (NI) soils had no history of irrigation and were selected based on textural and topographical similarities with the paired irrigated soils. The paired soils were from the same soil series and were <60 m apart at each sampling site. Soils were collected at discrete depth increments (0–5, 5–10, 10–20 cm), and samples were stored on ice during transport to the laboratory.

Soil Characterization

Soil samples were passed through a 2-mm sieve, and a subsample of the fine earth fraction was dried at 70°C for 1 wk. Particle size analysis was performed using the hydrometer method (Gee and Bauder, 1986) and organic matter (OM) was analyzed using a modified Walkley-Black procedure (Nelson and Sommers, 1982). Saturated pastes of air-dried soils (Rhoades, 1982) were centrifuged at 6000 g for 30 min and filtered (0.2 μ) prior to analysis for soluble constituents. Soluble Ca was analyzed using atomic absorption spectrophotometry (AAS), and soluble As was analyzed with continuous flow hydride generation atomic absorption spectrophotometry (HGAAS). Samples for As analysis were acidified to 3 M HCl, prereduced in 1% KI, and mixed in a reaction coil with 0.6% $NaBH_4$–0.5% NaOH. Flow rates were 7 and 1 mL min^{-1} for sample and reagent, respectively. Generated arsine was quantified in an air-acetylene flame (Perkin-Elmer 3100; Perkin-Elmer, Norwalk, CT) at 193.7 nm. Total soil As was analyzed using a four acid heat digestion (Welsch et al., 1990), and As levels in the resulting digests were quantified using HGAAS. Ammonium oxalate extractable (AOE) Fe, Mn, and Al were analyzed to estimate free oxide fractions (Loeppert and Inskeep, 1996), and Olsen P was extracted using the $NaHCO_3$ method of Olsen and Sommers (1982).

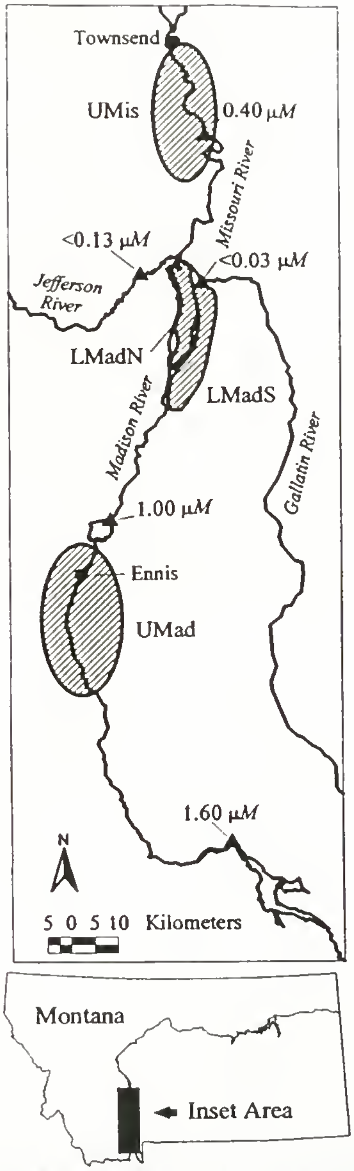

Fig. 1. Median surface water arsenic (As) concentrations (Nimick et al., 1998) and sampling locations in the Upper Madison (UMad; Sites A1-A4), Lower Madison South (LMadS; Sites B1-B4), Lower Madison North (LMadN; Sites C1-C4), and Upper Missouri (UMis; Sites D1-D4). Levels of As in the alluvial aquifer underlying the LMadN exceeded the federal drinking water standard of 0.67 μM As, yet were below this level in all other sampled ground water (Tuck et al., 1997).

Batch Sorption Isotherms

Soils from six paired sites (A1, B1, B4, C2, C3, D1) were selected for further analysis based on soluble and total As levels. Depth-weighted composites were formed by mixing the 0- to 5-cm, 5- to 10-cm, and 10- to 20-cm soil samples in a 1:1:2 mass ratio. Batch sorption isotherm experiments for As(V) were performed in duplicate, using a 2:1 solution:solid ratio (i.e., 20 mL 0.01 M KCl:10 g soil). Initial As concentrations were 0, 1.3, 4.0, 13, 40, 133, and 1330 μM, and each soil slurry was shaken on a horizontal shaker at approximately 120 cycles min^{-1} for 96 h. Equilibration time was determined by conducting a kinetic sorption study at 13 μM As using soils B1-NI and C2-NI. Samples were centrifuged at 10 000 g for

10 min, the supernatant filtered (0.2 μ), and the filtrate analyzed for As using HGAAS (described previously). Isotherm results were fit to Langmuir and Freundlich models, and r^2 values were found to be >0.999 for all 24 samples. Linear regressions also were performed, and the resulting distribution coefficients (K_d values), describing the linear portion of As sorption, were regressed against pH, O.M., clay content, AOE metals (Fe, Mn, Al), Olsen P, and total As.

A subsequent batch sorption experiment was conducted to determine the extent of As(V) reduction during the 96 h batch isotherm experiments. Initial As(V) concentrations of 0 and 13 μM were used for each of the 12 soils. As(V) and As(III) were determined using the following method modified from Masscheleyn et al. (1991b). Five milliliters of filtered sample was added to 0.5 mL of 2 M TRIS buffer (pH = 6.5). While bubbling this buffered solution with N_2 (g), a solution of 3% $NaBH_4$/0.1% NaOH was added incrementally (0.1 mL over 30 s, 3 min wait, 0.4 mL over 30 s, 3 min wait) to liberate arsine from any As(III) in the sample. The original sample (As(T)) and the speciated sample (As(V)) were both analyzed for As, and As(III) concentration was calculated by difference. Analysis of duplicate standards made from $NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$ salts yielded As(III) and As(V) recoveries of 97 ± 2% and 103 ± 1%, respectively.

Sequential Extractions

Paired surface soils (sites A1, C2, and C3), representing the full range of experimentally determined K_d values, were subjected to sequential extractions to estimate the distribution of soil-bound As based on a compilation of procedures (Johnston and Barnard, 1979; Tessier et al., 1979; Ganje and Rains, 1982; Olsen and Sommers, 1982). The method consisted of sequential extractions in the following order: 1 M NH_4Cl (exchangeable), 0.1 M NaOH (nonoccluded in Al and Fe oxides), 1 M HCl (Ca-bound and occluded in Al and Fe oxides), and 30% H_2O_2/0.8 M NH_4OAc (organically-bound). Although sequential extractions yield only qualitative information on As fractionation, this procedure helped assess relative As lability among irrigated and nonirrigated soils. Extracted samples were centrifuged at 10 000 g for 10 min and filtered through 0.2-μ nylon filters. The H_2O_2 extracts were analyzed for As with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and As in the remaining extracts was quantified with HGAAS. Total residual As was determined using heat digestion as described previously. Quality assurance–quality control consisted of the following: all samples were extracted in duplicate; percentage of recoveries were calculated by comparing summed extract concentrations with total As; interferences were tested by adding a known quantity of As to each C3-I extract (matrix spikes) and to each extraction blank (extraction spikes); HGAAS accuracy was assessed with USEPA certified standards obtained from Spex Certiprep (Metuchen, NJ). The mean relative standard deviation (RSD) of duplicate analyses that had As values above the detection limit was 11.4%. Total sequential extraction recoveries for the six samples averaged 95%, matrix spike recoveries ranged from 98 to 125%, extractant spike recoveries ranged from 96 to 109%, and the average recovery on duplicate USEPA standards was 99.5%.

Analysis for Solid Phases

Ion activity products (IAPs) for scorodite ($FeAsO_4 \cdot 2H_2O$) and $Ca_3(AsO_4)_2$ were calculated by assuming the activity of Fe^{3+} was controlled by an amorphous $Fe(OH)_3$(s) (log K_{sp} = −39.3) and that I = 0.013EC, where I = ionic strength in mol L^{-1} and EC = electrical conductivity in dS m^{-1} (Lindsay, 1979). Ion activities were calculated using the aqueous chemical equilibrium model, GEOCHEM (Sposito and Mattigod, 1979) as modified by Parker et al. (1987). Stability constants for relevant aqueous complexes were compiled from thermodynamic equilibrium data (Sadiq and Lindsay, 1979; Sposito and Mattigod, 1979; Nordstrom and May, 1990). Grains of sample C3-NI, the soil with the highest soluble and total As concentrations of the twelve chosen for further analyses, were affixed to Al stubs, coated with C, and viewed with a JEOL-6100 scanning electron microscope (SEM). The grains were mapped for As, Fe, Al, S, and Ca using energy dispersive analysis of x-rays (EDAX) and those grains containing elevated levels of As were more closely investigated to determine presence of discrete As solid phases.

Saturated Column Experiments

Column transport experiments were conducted on composited surface samples from soils B1-I, B1-NI, C2-I, and C2-NI to determine additional As sorption capacities. Both B1-I and C2-I had been flood-irrigated from 1882 to 1976 at approximately 60 cm yr^{-1}, and are currently sprinkler-irrigated at approximately 30 cm yr^{-1}. Soils were packed into acrylic columns (3 cm diam., 5 cm length) with final bulk densities of 1.15 to 1.25 g cm^{-3}. The soils were saturated from the bottom with 0.01 M KCl, then treated with influent (0.01 M KCl–1.3 μM As(V)) at a pore water velocity (saturated conditions) of 1.7 cm h^{-1} until the cumulative loading approached 900 cm (approximately 30 yr of simulated irrigation). Column effluent was passed through 0.45 μ in-line filters prior to sample collection and analysis. Effluent solution As concentrations were measured with HGAAS and the increase in soil As calculated by difference.

RESULTS AND DISCUSSION

Sample Characterization

Average total As levels in irrigated (I) soils were 1.5 to 3 mg kg^{-1} higher than in nonirrigated (NI) soils in both the Upper Madison (UMad; Sites A1–A4) and Lower Madison South (LMadS; Sites B1–B4); although neither difference was significant at α = 0.05 (Fig. 2). For comparison, total As levels in irrigated soils were estimated to be 1.5 to 7.5 mg kg^{-1} higher than in nonirrigated soils assuming 20 to 100 yr of irrigation at 60 cm yr^{-1}, an As concentration of 1 μM in irrigation water, 50% As retention in the upper 20 cm, and a bulk density of 1.5 g cm^{-3}. The measured differences in total As between irrigated and nonirrigated soils were within the range estimated in both UMad and LMadS soils, suggesting some retention of applied As in both regions. A reversed trend was observed in the Lower Madison North (LMadN; Sites C1–C4) where average total As levels were approximately 12 mg kg^{-1} lower in irrigated than in nonirrigated soils. Although the measured difference in As between irrigated and nonirrigated soils in the LMadN was not significant (α = 0.05), the lower As concentrations in irrigated soils suggest irrigation may be leaching As out of the soil profile. Total As concentrations in soils within the LMadN were two- to three-fold higher than in the other three sampling areas, again demonstrating the uniqueness of the LMadN region. The elevated As concentrations within the LMadN

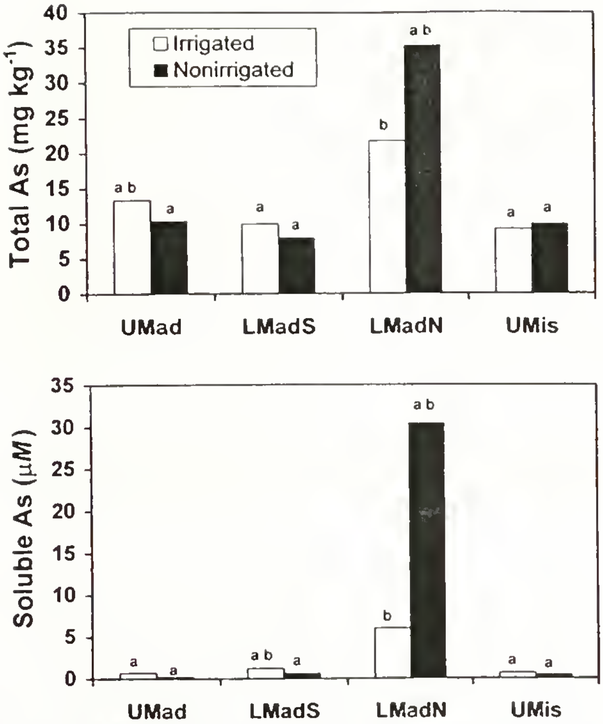

Fig. 2. Total and soluble As concentrations in the top 20 cm of soil for the Upper Madison (UMad), Lower Madison South (LMadS), Lower Madison North (LMadN), and Upper Missouri (UMis). Each value is an average of depth-weighted As levels from four sampling sites. Bars containing the same letter are not significantly different ($\alpha = 0.05$). The lack of significance between irrigated and nonirrigated As concentrations in the LMadN region is due to high variability among nonirrigated sites.

were clearly not caused by irrigation, but instead were apparently caused by natural conditions. For example, elevated concentrations of As in localized areas adjacent to the Madison and Missouri Rivers have been attributed to the presence of As-rich Tertiary volcanic sediments, sorption of river As to Fe oxides during flooding, and upward transport of reduced, As-rich ground water (Korte and Fernando, 1991; Nimick, 1998). Total As concentrations in the Upper Missouri (UMis; Sites D1-D4) were substantially lower than in the LMadN, and were more similar to As concentrations in the UMad and LMadS. Irrigated and nonirrigated soils in the UMis region had nearly identical total As concentrations, as expected due to relatively low As levels (~0.4 μ*M*) in irrigation water.

Soluble As concentrations followed the same trends as total As levels among regions and between irrigated and nonirrigated soils (Fig. 2). Most notably, average soluble As levels in nonirrigated soils of the LMadN were five-fold higher than in irrigated soils, suggesting that irrigation with lower Madison River water ([As] ~ 0.9 μ*M*) has decreased naturally occurring high levels of As by dilution and flushing. Average soluble As concentrations in the nonirrigated LMadN soils were approximately 30 μ*M*, more than 50-fold higher than concentrations in the other three nonirrigated areas (Fig. 2). In summary, although no significant ($\alpha = 0.05$) differences were found between irrigated and nonirrigated soils, UMad and LMadS soils may have sorbed some As from irrigation water, whereas naturally high levels of As in the LMadN have possibly been leached and diluted by irrigation water.

Table 1. Arsenic sorption coefficients (K_d) of six paired Madison River Valley soils.

Site	Linear K_d†	
	Irrigated	Nonirrigated
	L kg^{-1}	
A1	30.2 ± 1.0	33.2 ± 2.8
B1	7.9 ± 0.3	12.5 ± 1.7
B4	12.2 ± 0.02	8.2 ± 1.0
C2	3.4 ± 0.1	19.9 ± 0.1
C3	5.2 ± 0.7	17.7 ± 1.6
D1	29.3 ± 2.3	13.0 ± 0.8
Mean	14.7	17.4

† K_d values are from linear portions of duplicate isotherms.

Sorption of Arsenic in Irrigated vs. Nonirrigated Soils

Distribution coefficients (K_d), describing the linear portion of As sorption isotherms, ranged from 3.4 L kg^{-1} in C2-I to 33.2 L kg^{-1} in A1-NI (Table 1), indicating substantial differences in As sorption characteristics among soils. Although the mean K_d for irrigated soils was somewhat lower than for nonirrigated soils (14.7 ± 12.0 L kg^{-1} vs. 17.4 ± 8.8 L kg^{-1}), the difference was not significant ($\alpha = 0.05$). Therefore, irrigation has not significantly lowered the capacity for additional As sorption in the tested soils. A regression analysis between K_d and each of eight variables [pH, OM, clay content, AOE (ammonium oxalate extractable) metals (Fe, Al, Mn), Olsen P, and total As] was performed to determine which soil characteristics were correlated with As sorption. A three variable multiple linear regression described the majority of variation in K_d values among samples (Fig. 3). Colinearity was assessed between variables, and none of the three variables were significantly related ($\alpha = 0.05$). The equation

$$K_d = 0.015(\text{AOE Fe}) + 0.038(\text{AOE Mn}) - 0.62(\text{Olsen P}) + 3.3 \qquad (r^2 = 0.92)$$

suggests that levels of oxide materials and $NaHCO_3$-extractable P, rather than irrigation history, control As sorption in these soils. It has been well documented that As sorbs strongly to oxides of Fe (Hingston et al., 1971; Raven et al., 1998) and Mn (Oscarson et al., 1981), and that P competes for As sorption sites (Roy et al., 1986; Peryea, 1991; Darland and Inskeep, 1997a). Although irrigation could decrease As sorption by decreasing levels of Fe and Mn oxides, or increasing levels, there were no significant differences ($\alpha = 0.05$) between irrigated and nonirrigated means for any of these three variables (Table 2).

Determination of As(V) and As(III) species following the batch isotherm experiment revealed that >50% of the As(V) was reduced to As(III) in only C2-I and C3-I, the soils with the lowest K_d values. This suggests that K_d also may be a function of As valence state due to generally accepted differences in sorption between

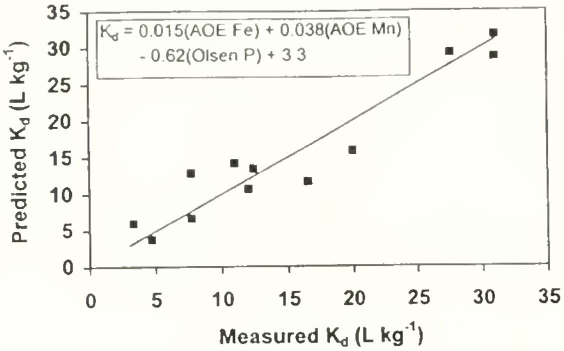

Fig. 3. Predicted versus measured K_d for 12 Madison River soils. Average measured K_d values were calculated from the linear portion of each duplicate sorption isotherm. The predicted K_d is based on a multiple linear regression with AOE (ammonium oxalate extractable) Fe, AOE Mn, and Olsen P (all with units of mg kg^{-1}) as independent variables.

As(V) and As(III) (Pierce and Moore, 1982; Xu et al., 1991); although it has recently been demonstrated that ferrihydrite can sorb similar amounts of As(III) and As(V) at high As surface coverages (Raven et al., 1998). When data from the two reduced samples were excluded from the regression analysis, the coefficients remained virtually the same, suggesting the production of As(III) in the two samples did not grossly affect the regression model. In summary, levels of oxide materials and $NaHCO_3$-exchangeable P apparently account for the majority of the variability in K_d values among soils.

Partitioning of Arsenic in Selected Soils

Irrigation has not consistently altered the partitioning of As in three soils from the Upper and Lower Madison regions based on a comparison of sequential extraction data between irrigated and nonirrigated soils (Fig. 4). More notable differences in As partitioning and lability exist between sites. For example, the 1 *M* NH_4Cl and 0.1 *M* NaOH fractions account for approximately 10 mg kg^{-1} in both C3-I and C3-NI, yet <2.5 mg kg^{-1} in the other four soils. These differences in the two most labile fractions are consistent with the high soluble As concentrations found in C3-I (12 μ*M*) and C3-NI (20 μ*M*) compared with soluble As concentrations of <3 μ*M* found in the other four soils. In addition, residual fractions account for <20% of the total As in C3, yet approximately 50% of total As in A1 and C2, also indicating large differences in As lability between sites. Soils from C2 and C3 are both from the LMadN region, again demonstrating the high degree of heterogenity in As distribution within this region. In summary, irrigation history has not substantially altered As distribution at three selected sites.

Table 2. Average chemical and physical characteristics† from the top 20 cm of six paired Madison River Valley soils.

Parameter	Irrigated	Nonirrigated	*P*-value	Significance
K_d, L kg^{-1}‡	14.7 ± 12.0	17.4 ± 8.8	0.66	NS§
pH	8.0 ± 0.1	8.0 ± 0.2	0.51	NS
OM, %	2.8 ± 1.9	3.1 ± 2.7	0.79	NS
Clay, %	20.7 ± 9.1	17.3 ± 8.5	0.56	NS
AOE¶ Fe, mg kg^{-1}	656 ± 479	455 ± 162	0.35	NS
AOE Mn, mg kg^{-1}	292 ± 163	322 ± 179	0.77	NS
AOE Al, mg kg^{-1}	828 ± 246	789 ± 277	0.80	NS
Olsen P, mg kg^{-1}	15.3 ± 9.2	8.3 ± 3.0	0.11	NS
Total As, mg kg^{-1}	14.9 ± 7.9	20.0 ± 21.1	0.59	NS

† The pH, OM, clay, and total As values are depth-weighted averages (Keith, 1995), and the remaining results are for depth-weighted composites.

‡ K_d values were calculated from the linear portion of duplicate isotherms.

§ NS, Not significant (α = 0.05).

¶ AOE, Ammonium oxalate extractable (Loeppert and Inskeep, 1996).

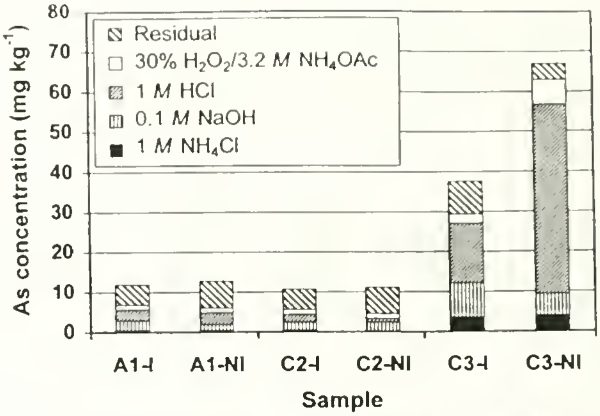

Fig. 4. Concentrations of As recovered from each sequential extractant for three irrigated (I) and nonirrigated (NI) soils. Values are averages of results from extractions performed on duplicate samples.

Ion activity products (IAPs) calculated for the upper three depth increments (0–5, 5–10, and 10–20 cm) of each soil were compared with K_sp values (Wagemann, 1977) for $Ca_3(AsO_4)_2$ and scorodite ($FeAsO_4 \cdot 2H_2O$). IAPs were lower than *K*sp values by at least six and nine orders of magnitude for $Ca_3(AsO_4)_2$ and scorodite, respectively, indicating saturated pastes from these soils were undersaturated with respect to both solid phases. Given inconsistencies in literature K_{sp} values (Sadiq and Lindsay, 1981), and uncertainty that true equilibrium was reached during the 24 h saturated paste extraction, it cannot be definitively concluded from IAP calculations that metal arsenates did not exist in these samples. Although insufficient data were available to test for presence of other metal arsenates, analysis of C3-NI using SEM-EDAX revealed no solid phases concentrated in As. The saturation indices coupled with the SEM-EDAX observations suggest that discrete metal arsenate phases were not controlling aqueous As activities. Therefore, sorption–desorption reactions rather than precipitation–dissolution reactions probably control As levels in soils of the study area.

Saturated Column Experiments

The two soils (B1 and C3) chosen for saturated column experiments had been irrigated for approximately 110 yr with As-rich Madison River water; yet both soils had additional capacities to retain As. Soil As concentrations increased between 3 (C2-I) and 7.5 mg kg^{-1} (C2-NI) following approximately 900 cm of cumulative loading with a 1.33 μ*M* As influent (Fig. 5). Soil C2-I had the lowest K_d (3.4 L kg^{-1}) of the 12 soils selected for further analysis (Table 1); therefore, 3 mg kg^{-1} likely

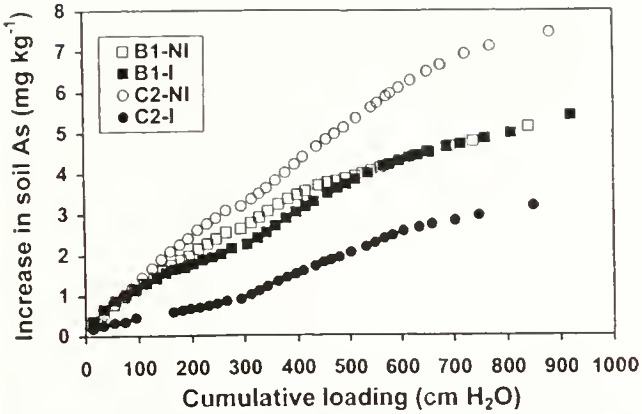

Fig. 5. Increase in soil arsenic as a function of water loading in saturated soil columns (5 cm long, 3 cm diam.). Influent (1.33 μM As in a 0.01 M KCl background solution) was pumped at a pore water velocity of 1.7 cm h^{-1} in both irrigated (I) and nonirrigated (NI) soil columns.

represents the lower boundary of additional As retention capacities in these soils. Increases in soil As in the saturated column experiments appeared to be positively related to 96 h batch K_d values, suggesting that As retention observed in the column experiments also was controlled by levels of oxide materials and Olsen P. Removal efficiencies of As during the first five pore volumes ranged from 48 (C2-I) to 85% (B1-I); however, by the end of this experiment, the soils were removing <22% of the influent As. The total mass of As attenuated under field conditions will be higher because the column experiments were only performed with 5 cm columns. Differences in pore water velocity (PWV) between this experiment (PWV = 1.7 cm h^{-1}) and field conditions also may have a large effect on As transport. In a packed sand column (Darland and Inskeep, 1997b), As recovery in the effluent after 10 pore volumes was 7.2, 35.6, and 53.3% at PWVs of 0.2, 1, and 10 cm h^{-1}, consistent with sorption-related nonequilibrium. Therefore, PWVs are expected to affect As attenuation, and actual As retention is expected to be higher than measured due to anticipated slower average pore water velocities in the field. In addition, anticipated flow conditions in the field (transient, unsaturated flow) are expected to result in greater As removal, compared to laboratory column experiments (steady-state, saturated flow). Conversely, there is a lower likelihood for preferential flow in column experiments due to generally fewer macropores in repacked soil columns compared with field conditions. Despite differences between laboratory and field conditions, the column transport studies on soils from sites B1 and C2, combined with earlier results (Darland and Inskeep, 1997b), support the contention that As transport in these soils is likely controlled by As sorption to oxide materials and pore water velocities.

CONCLUSIONS

Soils adjacent to the Madison and Missouri River Valley were studied to determine if long-term irrigation was affecting soil profile As levels, sorption coefficients, lability, or mobility. Total and soluble As levels in the upper soil profile (top 20 cm) were slightly higher in irrigated soils than in nonirrigated soils of the Upper Madison and Lower Madison South regions, suggesting some retention of applied As. This observed trend was reversed in the Lower Madison North where average soluble and total As levels were 6- and 1.5-fold higher, respectively, in nonirrigated soils than in irrigated soils. The differences imply that irrigation has lowered naturally-occurring high levels of As in soils from the Lower Madison North through dilution and flushing. Average sorption coefficients were 16% lower in irrigated than in nonirrigated soils although this difference was not significant (α = 0.05). Sorption coefficients were positively correlated with measured levels of free Fe and Mn oxides, and negatively correlated with NaHCO$_3$-extractable P. Therefore, dissolution of oxides or additional inputs of P would both be expected to decrease As sorption. Sequential extractions showed no major increases in labile As between irrigated and nonirrigated soils, consistent with solution As data. Saturated transport studies demonstrated that surface soils that have been irrigated with As-rich water for >100 yr have additional As sorption capacities of at least 3 mg kg^{-1}, and these capacities are positively correlated with sorption coefficients. Although As removal efficiencies fell from >48% to <22% following 30 yr of simulated irrigation in 5-cm columns, attenuation of As is expected to be higher in the field due to deeper soil profiles and slower average pore water velocities. In summary, soil profile As levels and sorption characteristics have not been significantly affected by up to 110 yr of irrigation with As-rich Madison and Upper Missouri River water. Due to the large variability in soil profile As levels and sorption capacities between sampling sites, potential impacts from irrigation projects should be assessed on a site-specific basis.

ACKNOWLEDGMENTS

This work was funded by the Montana Department of Natural Resources and Conservation, the Montana Water Center, and the Montana Agricultural Experiment Station. We thank Jeffrey Darland (Oregon Graduate Institute, Beaverton, Oregon) for conducting the saturated column studies, and Chuck Dalby (Department of Natural Resources and Conservation, Helena, MT) and David Nimick (U.S. Geological Survey, Helena, MT) for project collaboration and manuscript review.

REFERENCES

Darland, J.E., and W.P. Inskeep. 1997a. Effects of pH and phosphate competition on the transport of arsenate. J. Environ. Qual. 26:1133–1139.

Darland, J.E., and W.P. Inskeep. 1997b. Effects of pore water velocity on the transport of arsenate. Environ. Sci. Technol. 31:704–709.

Davenport, J.R., and F.J. Peryea. 1991. Phosphate fertilizers influence leaching of lead and arsenic in a soil contaminated with lead arsenite. Water Air Soil Pollut. 57–58:101–110.

Dove, P.M., and J.D. Rimstidt. 1985. The solubility and stability of scorodite, FeAsO$_4$ · 2H$_2$O. Am. Mineral. 70:838–844.

Eary, L.E. 1992. The solubility of amorphous As$_2$S$_3$ from 25 to 90°C. Geochim. Cosmochim. Acta. 56:2267–2280.

Frost, R.R., and R.A. Griffin. 1977. Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals. Soil Sci. Soc. Am. J. 41:53–57.

Ganje, T.J., and D.W. Rains. 1982. Arsenic. p. 385–402. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. p. 383–411. *In* A. Klute (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Goldberg, S., and R.A. Glaubig. 1988. Anion sorption on a calcareous, montmorillonitic soil-arsenic. Soil Sci. Soc. Am. J. 52:1297–1300.

Hingston, F.J., A.M. Posner, and J.P. Quirk. 1971. Competitive adsorption of negatively charged ligands on oxides surfaces. p. 334–343. *In* F.C. Tompkins (ed.) Surface chemistry of oxides. Discussions of the Faraday Soc. no. 52. The Faraday Soc., London.

Jones, C.A., W.P. Inskeep, and D.R. Neuman. 1997. Arsenic transport in contaminated mine tailings following liming. J. Environ. Qual. 26:433–439.

Johnston, S.E., and W.M. Barnard. 1979. Comparative effectiveness of fourteen solutions for extracting arsenic from four western New York soils. Soil Sci. Soc. Am J. 43:304–308.

Keith, K.E. 1995. Arsenic in soils of the Madison and upper Missouri River valleys. M.S. thesis. Dep. of Plant and Soil Science, Montana State Univ., Bozeman.

Korte, N.E., and Q. Fernando. 1991. A review of arsenic(III) in groundwater. CRC Crit. Rev. Environ. Control. 21:1–39.

Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley & Sons, New York.

Loeppert, R.H., and W.P. Inskeep. 1996. Iron. p. 639–664. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. SSSA Book Ser. no. 5. ASA and SSSA, Madison, WI.

Masscheleyn, P.H., R.D. Delaune, and W.H. Patrick, Jr. 1991a. Arsenic and selenium chemistry as affected by sediment redox potential and pH. J. Environ. Qual. 20:522–527.

Masscheleyn, P.H., R.D. Delaune, and W.H. Patrick, Jr. 1991b. A hydride generation atomic adsorption technique for arsenic speciation. J. Environ. Qual. 20:96–100.

McGeehan, S.L., and D.V. Naylor. 1994. Sorption and redox transformations of arsenite and arsenate in two flooded soils. Soil Sci. Soc. Am J. 58:337–342.

Nelson, D.W., and L.E. Sommers. 1982. Organic carbon. p. 539–579. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Nimick, D.A. 1998. Arsenic hydrogeochemistry in an irrigated river valley: A reevaluation. Ground Water. 36(5):743.

Nimick, D.A., J.N. Moore, C.E. Dalby, and M.W. Savka. 1998. The fate of geothermal arsenic in the Madison and Missouri Rivers, Montana and Wyoming. Water Resour. Res. 34:3051–3067.

Nishimura, T., C.T. Itoh, and K. Tozawa. 1987. Stabilities and solubilities of metal arsenites and arsenates in water and effect of sulfate and carbonate ions on their solubilities. p. 77–98. *In* R.G. Reddy et al. (ed.) Proc. of the Symp. on Arsenic Metallurgy, Fundamentals and Applications, Phoenix, AZ. 25–29 Jan. 1988. Metallurgical Soc., Warrendale, PA.

Nordstrom, D.K., and H.M. May. 1989. Aqueous equilibrium data for mononuclear aluminum species. p. 29–53. *In* G. Sposito (ed.) The environmental chemistry of aluminum. CRC Press, Boca Raton, FL.

Olsen, S.R., and L.E. Sommers. 1982. Phosphorus. p. 403–430. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Oscarson, D.W., W.K. Liaw, and P.M. Huang. 1981. The kinetics and components involved in the oxidation of arsenite by freshwater lake sediments. Verh. Internat. Verein. Limnol. 21:181–186.

Parker, D.L., L.W. Zelazny, and T.B. Kinraide. 1987. Improvements to the program GEOCHEM. Soil Sci. Soc. Am. J. 51:488–491.

Peryea, F.J. 1991. Phosphate-induced release of arsenic from soils contaminated with lead arsenic. Soil Sci. Soc. Am. J. 55:1301–1306.

Pierce, M.L., and C.B. Moore. 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Res. 16:1247–1253.

Raven, K.P., A. Jain, and R.H. Loeppert. 1998. Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. Environ. Sci Technol. 32:344–349.

Rhoades, J.H. 1982. Soluble salts. p. 167–179. *In* A.L. Page (ed.) Methods of soil analysis. Part 2. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Robins, R.G. 1981. The solubility of metal arsenates. Metallurgical Trans. B. The Am. Soc. for Metals and The Metallurgical Soc. of AIME. 12B:103–109.

Roy, W.R., J.J. Hassett, and R.A. Griffin. 1986. Competitive interactions of phosphate and molybdate on arsenate adsorption. Soil Sci. 142:203–210.

Sadiq, M., T.H. Zaidi, and A.A. Mian. 1983. Environmental behavior of arsenic in soils: Theoretical. Water Air Soil Pollut. 20:369–377.

Sadiq, M., and W.L. Lindsay. 1979. Selection of standard free energies of formation for use in soil chemistry. Tech. Bull. 134. Colorado State Univ. Exp. Stn., Fort Collins.

Sadiq, M., and W.L. Lindsay. 1981. Arsenic supplement to technical bulletin 134: Selection of standard free energies of formation for use in soil chemistry. Colorado State Univ. Exp. Stn., Fort Collins.

Sonderegger, J.L., and T. Ohguchi. 1988. Irrigation related arsenic contamination of a thin alluvial aquifer, Madison River Valley, Montana, U.S. Environ. Geol. Water Sci. 11:153–161.

Sposito, G., and S.V. Mattigod. 1979. A computer program for the calculation of chemical equilibrium in soil solutions and other natural water systems. Kearney Foundation of Soil Sci., Univ. of California, Riverside.

Stauffer, R.E., and J.M. Thompson. 1984. Arsenic and antimony in geothermal waters of Yellowstone National Park, Wyoming, U.S.A. Geochim. Cosmochim. Acta. 48:2547–2561.

Tessier, A., P.G.C. Campbell, and M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51(7):844–851.

Tuck, L.K., D.M. Dutton, and D.A. Nimick. 1997. Hydrologic and water-quality data related to the occurrence of arsenic for areas along the Madison and upper Missouri Rivers, southwestern and west-central Montana. USGS Open-File Rep. 97-203. Helena, MT. U.S. Geological Surv., Denver, CO.

Wagemann, R. 1977. Some theoretical aspects of stability and solubility of inorganic arsenic in the freshwater environment. Wat. Res. 12:139–145.

Waychunas, G.A., J.A. Davis, and C.C. Fuller. 1995. Geometry of sorbed arsenate on ferrihydrite and crystalline FeOOH: Re-evaluation of EXAFS results and topological factors in predicting sorbate geometry, and evidence for monodentate complexes. Geochim. Cosmochim. Acta. 59:3655–3661.

Webster, J.G. 1990. The solubility of As_2S_3 and speciation of As in dilute and sulphide-bearing fluids at 25 and 90°C. Geochim. Cosmochim. Acta. 54:1009–1017.

Welsch, E.P., J.G. Crock, and R. Sanzolone. 1990. Trace-level determination of arsenic and selenium using continuous-flow hydride generation atomic absorption spectrophotometry (HG-AAS). *In* B. Arbogast (ed.) Quality assurance manual for the branch of geochemistry, USGS Open-File Rep. 90-688. U.S. Geological Surv., Denver, CO.

Xu, H., B. Allard, and A. Grimvall. 1991. Effects of acidification and natural organic materials on the mobility of arsenic in the environment. Water Air Soil Pollut. 57–58:269–278.